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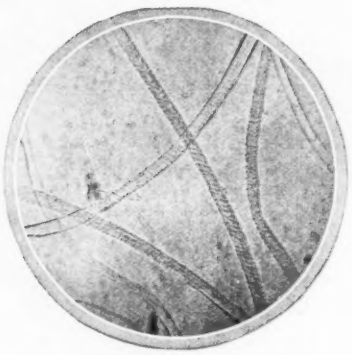
These textile fibres were processed in the ordinary water supply of a well known mill. Under the microscope note the sticky deposits clinging to the fibres. In the finished goods these deposits will show up as a defect. (From an unretouched photomicrograph.)



These textile fibres are exact duplicates of those to the left, except that they were processed in Permutit conditioned water. Note how smooth and clean the fibres are. (From an unretouched photomicrograph.)

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HAS it ever occurred to you that water is your biggest raw material—that it should be studied and examined for impurities just as you inspect other raw materials?

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Think for a minute of the course water takes before reaching your mill, and you will see why this is true. Water is the greatest solvent in the world. When it falls on the earth as rain, it soaks into the ground. It runs over earth, rocks, minerals and decomposing vegetable matter. It flows into rivers, lakes and streams. Eventually, it reaches your plant.

But in its course your water supply has dissolved and carried along many substances that have no place in textile manufacturing. Substances that easily upset the delicate chemical and physical balance of your operations. You may go along for years without suspecting the presence of these substances, or the true cause of many production difficulties. Just as did the mill that sent us the two photomicrographs above.

This mill is nationally known. For years it had about the same number of rejections and troubles as other mills. Finally it consulted the Permutit Company, water conditioning specialists, with the result shown in the photographs above.

That to the left shows textile fibres treated in the mill's ordinary water supply. The sticky lime deposits clinging to the fibres were deposited there by the water. They will show up as a defective spot in the finished goods. After Permutit water conditioning apparatus was installed, the fibres came through clean and smooth as you see them on the right.

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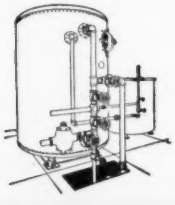
You should have a copy of our booklet, "Reducing Textile Costs and Troubles." It goes fully into the subject of textile mill water supply from the standpoint of what the experience of other mills has been. Send for a free copy today, there is no obligation.



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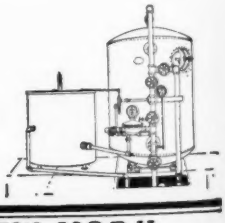

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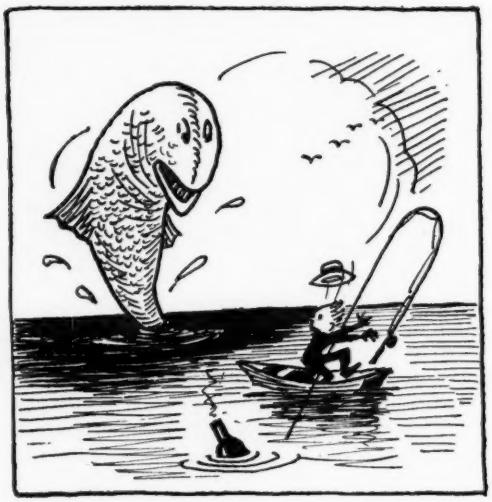

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VOLUME XV NEW YORK, SEPTEMBER 20, 1926 No. 16

Corrosion of Nickel-Alloy Singe Rolls

Selection of Metal for Singeing Rolls—Corrosion from Sizing Compounds—Tests Made on Nickel-Alloy—Objections to Use of Certain Ingredients—The Apparatus

By JOHN T. TRAVIS

American Gas Furnace Company, Elizabeth, N. J.

"ETERNAL vigilance," we are told, "is the price of liberty," and this is especially applicable to conditions in the textile industry to-day.

During the past decade, efforts by makers of the equipment used in the manufacturing and converting of textile fabrics, have been largely directed to the unification of processing (this being necessitated by steadily increasing labor costs), and the economizing on fuel consumption costs whenever and wherever possible.

It is a well-known fact that although to-day production costs are relatively high, selling prices of practically all staple textile fabrics are disproportionately low.

Mass production on a further reduced cost basis seems therefore the most ready and practical solution of our present industrial problem.

To effect this, modernizing of processing by every available means seems to be absolutely necessary, if the textile industry is to meet the conditions as at present imposed, and as evidenced by the reduction or total elimination of marginal profits.

Among the many improvements effected during the past few years by makers of modern finishing equipment and auxiliary appliances, a noteworthy and economical application has been shown in the rotary plate method of singeing cotton cloth.

The selection of a metal suitable for service at high temperatures is of prime imporance, as it is highly advisable that no oxidation of the metal occurs during the passage and contact of the cloth through the singeing process.

A special nickel-alloy metal is used for this purpose, its chief characteristics being its high heat-resisting properties, and freedom from oxidation at singeing heat which, to be thoroughly effective, should be uniformly maintained at approximately 1,400 deg. Fahr.

To meet varying conditions as to moisture content of cloth, its weight, density, etc., a heating capacity of the singe roll far in excess of the average should be possible, and, in turn, should be effectively controlled.

To run a steam engine without governors would be quite as consistent as to attempt the operation of modern heating appliances efficiently with manual control.

Uniformity of singeing is of prime importance and this cannot be produced with varying service as to heat, and without even tension and uniform contact of the cloth.

Installations of the rotary singers, equipped with gas-heated nickel-alloy metal rollers, have been made by a number of the leading converters of cotton fabrics, and the value of such apparatus is proved by the fact that among the present users are many firms well known for the excellence of their product.

A number of these rollers now in use at various plants show some corrosion of the alloy metal, and for some time intensive research work has been conducted by metallurgical and other chemists, in an effort to arrive at a satisfactory understanding as to the exact cause of the disintegration of the metal.

Corrosion from Sizing Compounds

These efforts have at last been successful, and tests have shown conclusively that the corrosion is entirely due to the fact that ingredients in the sizing compounds used by many cloth manufacturers are responsible for this unsatisfactory result.

None of the baser metals would withstand the attack under such conditions as are necessarily present

in efficient singeing operations of the ingredients referred to, which may operate injuriously alike on both the metal and the fabric.

As it is possible to maintain considerably higher temperatures on the rotary singers than can be obtained in any other known method of singeing, it is very natural to conclude that this has forced results not readily apparent in other singeing applications, as high heat intensity is required to effectively decompose the objectionable compound.

It is interesting to note also that in the event this reaction does not occur in the singeing process, through lack of heat intensity, the subsequent result would be the neutralizing of the desizing liquor used in the cleansing of the fabric after singeing, as the enzymes would be destroyed and poor results in the desizing of the fabric be shown.

As one of the chief reasons for the use of this ingredient is to prevent mildew of the cloth it naturally follows that any agent capable of preventing fermentation in one period will have the same effect subsequently if the preventive agent has not meanwhile been removed or its effects nullified.

The ingredient referred to in the foregoing is zinc chloride, and the equation showing the reaction, when subjected to intense heat, is as follows:

$$ZnCl_2 + H_2O = 2HCl + ZnO$$

From this it is clearly evident that on the application of the heat from the singe roll the hydrochloric acid is vaporized and the zinc-oxide is precipitated.

The rotary singer, being more efficient as to heating capacity, very naturally affects the zinc chlorides more effectually than would be the case were singeing done at lower temperatures.

The chief reasons for the use of zinc chloride in warp-sizing compounds are:

Prevention of mildew in goods shipped or stored in the gray.

Hygroscopic feature prevents size hardening in weaving process.

Hygroscopic features and weight of zinc add weight to woven fabric.

It has recently been brought directly to the writer's notice that one of the leading manufacturers has prohibited the use of this ingredient on account of the trouble experiences in their converting department directly attributable to this cause.

A number of converters have previously had trouble of a like nature and the use of zinc chloride is discouraged by them for the purpose referred to, viz., as an ingredient in the sizing compound.

Tests Made on Nickel-Alloy

Having by definite tests fully determined that the trouble experienced in the corrosion of the alloy metal is attributable to the use of zinc chloride in the warp-sizing compounds used by weavers, the singe rollers cannot be guaranteed against corrosion, unless some method is followed by converters to counteract this objectionable ingredient.

As zinc chloride is readily soluble in water, a washing previous to singeing would readily remove it, and this is recommended on any fabrics which are found to contain this ingredient in the warp-size.

Zinc-oxide is insoluble in water, and to this fact many troubles experienced by finishers may be attributed as, once it is precipitated, it is difficult to remove and will tend to dull and cloud the color and impair the finish and luster of the cloth.

For the scientific data as used in connection with the foregoing, and its practical application, the writer is indebted to P. J. Wood, manager of the Oriental Silk Printing Company, Haledon, N. J., who is a recognized authority on chemistry, particularly as applied in the textile trade.

While the effects must be deplored, so far as the singe rolls are concerned, the greatest interest will be manifested by readers as to the results on the fabrics processed. The singe roller may be replaced at comparatively low cost after a lengthy period of service, but tender goods are a total loss to the converter.

Tests of the nickel-allow metal included immersion of the metal in muriatic acid at atmospheric temperature, and also immersion of the metal while heated to about 1,350 to 1,400 deg. Fahr., which is the average heat used on rotary singers.

Practically no corrosion occurred on the metal while immersed in muriatic acid for a period of 170 hours at atmospheric temperature for both metal and acid.

A frequent immersion of the metal while heated to about 1,350 to 1,400 deg. Fahr., in muriatic acid at atmospheric temperature, resulted in a very appreciable corrosion of the metal within a two-hour period, thus confirming the theory that the heat greatly accelerates the corrosion of the metal.

The fact should be particularly emphasized that there is no middle course to pursue in any effort to avoid the results consequent on the use of zinc chloride, and that the findings have been more readily made possible on account of the fact that the rotary type of singer is more highly efficient as to heating qualities and therefore shows the fullest reaction of the zinc chloride.

To singe the fabric at lower heat would merely prevent the complete decomposition of the zinc chloride, and the consequent result would be poor singeing and unsatisfactory desizing of the fabric in the after processes.

In the issue of The Reporter, June 30, 1924, Vol. XIII, No. 11, appaers an article written by Charles F. Goldthwait on the subject, "Acid in Cotton Goods," and this treats conclusively on the results of hydrochloric acid content in cotton fabrics, and refers to tests made at much lower temperatures than used in any efficient singeing operations.

The writer but recently observed this, subsequent to tests being made as referred to above, and the following quotation is of especial interest:

> Their (Coward, Wood and Barrett's) conclusion was that 0.01 per cent of hydrochloric acid will cause appreciable tendering at 120 deg. Cent. (248 deg. Fahr.) and that 0.05 per cent will produce bad tendering even at 100 deg. Cent. (212 deg. Fahr.)

Further:

> Another remark of unknown source that "As little as 0.002 per cent of acid in cotton cloth is dangerous, and even 0.01 per cent will cause tendering if pressed with a very hot iron," referring particularly to sulphuric acid such as might develop in sulphur dyed goods.

Objections to Use of Certain Ingredients

The information available seems to indicate that many converters and textile chemists are opposed to the use of this harmful ingredient and that some steps should be taken to thoroughly discourage its use by cloth manufacturers.

From Bean's "Chemistry and Practice of Finishing," published in 1905, the following quotations are of interest:

> *The Size.*—This should not contain anything more than starchy and fatty matters, although cloth intended for bleaching frequently contains, in addition, the chlorides of zinc, magnesium, and calcium, China clay, and paraffin wax. The use of these latter substances cannot be too strongly condemned, and their more objectionable features will be further discussed.
>
> *Chloride of Zinc.*—This is added to the size to prevent mildew. It is an unnecessary ingredient as mildew should be avoided by correct drying during the process of taping, and afterward by careful storage.
>
> *Chloride of Magnesium.*—This is used in the size to obtain better weaving. It strengthens the fibers by its power of absorbing moisture, and on this account the manufacturer has less breakage and better production. It is, however, a most dangerous substance to use when the cloth has to be bleached, on account of its tendency to decompose, when heated, into free hydrochloric acid and free hydrate of magnesium, with a consequent tendering of the fiber; this decomposition takes place during the process of singeing.
>
> *Chloride of Calcium.*—This is not often used as a sizing ingredient. Its powers of attracting moisture are similar to those of chloride of magnesium, and where a deliquescent substance is necessary, it would be far less dangerous to use than the magnesium salt, as it is not easily decomposed by heat.

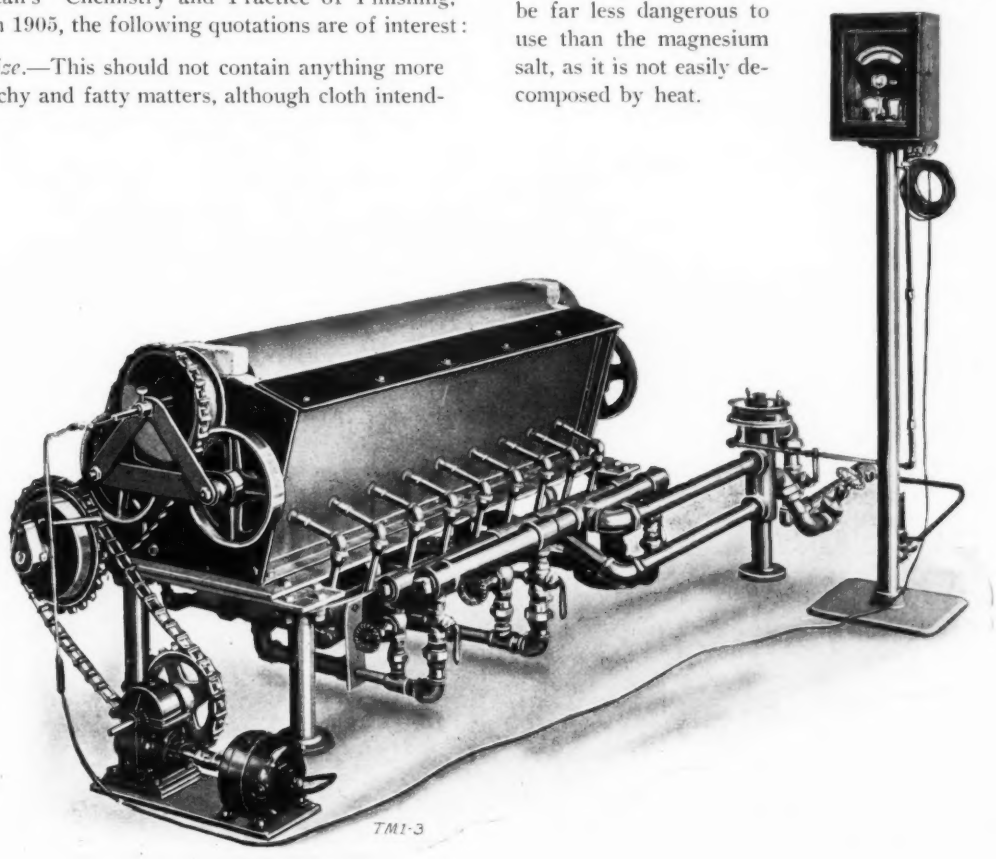

Fig. 1

Paraffin Wax.—This is most objectionable substance to have present in cloth intended for bleaching. It is not easily removed in the processes of washing and scouring, and may give rise to stains after the cloth is bleached.

Chlorine decomposes paraffin wax, producing a substance which resists the dyes. Where goods have to be dyed or printed, the presence of paraffin wax prevents the colors spreading evenly.

It is thus evident that chlorides have long been objectionable for use in sizing compounds to the most eminent chemists whose judgment on such matters remains undisputed.

The following extract from a circular issued by a well-known dealer in desizing products will serve to explain the difficulty of satisfactorily cleansing the singed fabric, if this has been treated with zinc-chloride and has not been washed previous to singeing:

> When the finishing plant complains to the gray goods mill, it is usually the case that mineral salt or some moisture absorbent has been used in a compound in the size box to increase moisture in weaving. This is especially noticeable in the finishing of piece dye twills and drills, which require singeing. Passing over the flame of the singeing machine, due to the chloride content in the warp yarn, hydrochloric acid is formed, retarding the energy of the enzyme (malt-diastase) or killing it. Failing in its work, the pursuant washing will not remove all of the warp size, creating stiff blotches, which, coming in contact with the dyestuff, cause streaking.

In a booklet recently issued by Chemical and Metallurgical Engineering on the subject of "Combating Corrosion in Industry," are noted the following references on pages 79 and 117, relative to the destructive qualities of Hydrochloric Acid:

> When the chemical engineer tackles hydrochloric acid, whether for its manufacture or use, he comes closer to hearing the jaws of the corrosion dragon snap than at any other time. Whether present in vapor or liquid phase and whether pure or impure, the substance has few equals for the viciousness with which it attacks materials of construction.
>
> Hydrochloric acid slowly dissolves nickel and most of its alloys. It is used as an etching reagent for this metal in metallographic work. The presence of an oxidizing agent accelerates corrosion.

The Apparatus

So far as it has been possible to ascertain, no corrosion of the nickel-alloy metal occurs in the singeing of cotton fabrics which have not been treated with chloride in the warp-sizing process, and as zinc chloride is readily soluble in water at a temperature of 100 deg. Fahr., a washing prior to singeing would prevent the tendering of the fabric, and the corrosion of the singe roll, and also insure more satisfactory cleansing of the fabric in the desizing process after singeing.

The illustration (Fig. 1), will serve to show the most modern type singeing equipment referred to in the foregoing as the Gas Fired Rotary Plate Singer, operated in either single or double units, and arranged to singe either one or both sides of the cloth in one operation.

The drawing (Fig. 2) shows the general arrangement of the entire run of the cloth from the gray room to the bin or plaiting-down apparatus, and in the event that the drying of the fabric after washing cannot be done at the speed suitable for singeing, a break in the run before entering the slack-box would be necessary.

A peculiar feature in the corrosion of alloy metals may be noted and be of interest to the reader.

Various metals, nickel, chromium, etc., enter into the composition of the alloy, and after varied resistance to the action of the acid.

The metal offering the least resistance is completely decomposed or corroded before the acid affects any of the other metals which enter into the composition of the complete alloy, after which the metal next in order of

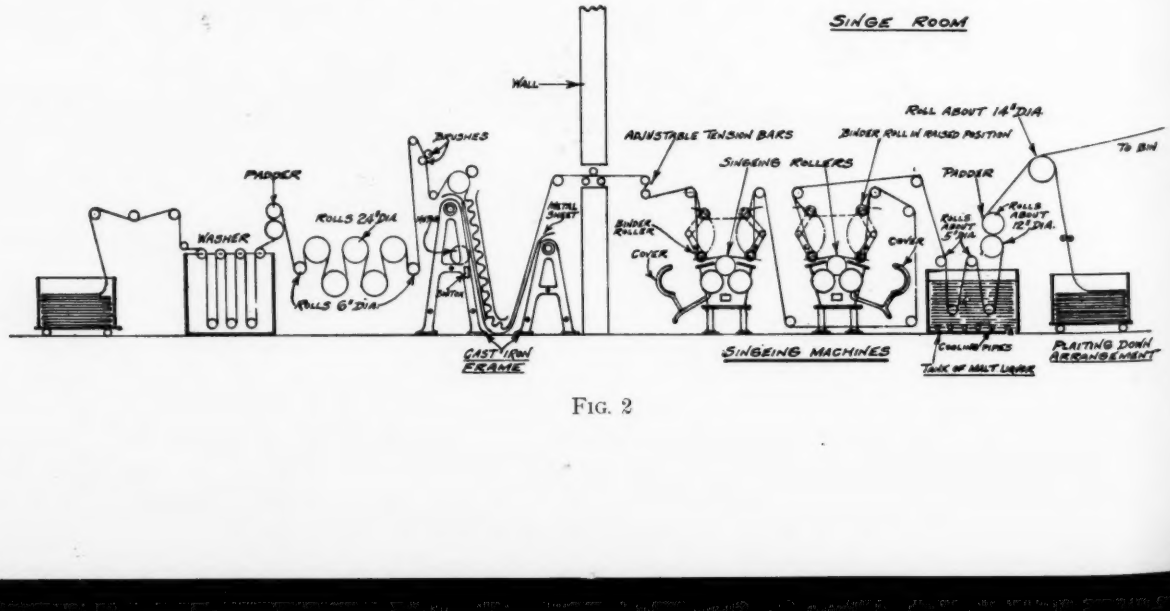

FIG. 2

sensitiveness is attacked, and this corrosion will continue until all of the metals have become decomposed.

This explains why the alloy metal becomes "honeycombed," and the casting is made exceedingly porous by the action of hydrochloric acid when subjected to intense heat in the singeing process.

It may interest readers to know that even under the adverse conditions referred to, one of these alloy metal rollers was recently replaced after about sixteen months' continuous service at about 1,400 deg. Fahr., and this roll, re-ground, will be capable of giving still further service.

With the corroding influence removed, more complete satisfaction may be obtained by the user.

Textile Dyeing

Dyeing Process—Dyestuffs—Dyeing Aids—Dyeing Formulas—Equipment—Dyeing Artificial Silk and Wool

By W. K. ROBBINS

Manchester, N. H.

WHEN the American Chemical Society was born the colors available for the textile industry were few in number, dull in shade, and applied with varying success to the different fibers then used. Fastness was unsatisfactory and the dyer followed empirical methods both laborious and tedious. The dyes were derived principally from the vegetable kingdom and the extraction of the dyestuff yielded a mixture containing substances other than the dye, some of which may have helped but most of which hindered the application of the color. The formulas used in the dyehouse were derived by hit-and-miss experimentation and were considered profound secrets; even the men carrying out the process were not permitted to know with what they worked nor why they proceeded in a particular way.

Dyeing Process

Most of the dyes in use at that time formed combinations with wool, which absorbs the color from aqueous solutions so completely as to exhaust the dye bath. These dyes are not removed by washing, though treatment with metallic salts improves their fastness and modifies the shade. For these reasons wool has long been dyed in the fiber or loose state as well as in the form of yarn cloth, and the introduction of modern dyestuffs has on the whole brought about comparatively few changes in equipment and methods of handling this fiber.

Cotton, having no such affinity for the natural dyestuff used on wool, was a source of much trouble to the dyer fifty years ago. Cotton is able to take up tannin, but no stable combination is formed and it is readily washed out. If, however, the dyed fiber is treated, without rinsing, with a metallic salt such as those of tin, antimony, and iron, the color adheres sufficiently to resist moderate washing. Most of the colors derived from dyewoods are in combination with tannin and therefore, with the use of mordants, became fixed upon the fibers, but the process was accompanied with a considerable precipitation of the color not attached directly to or absorbed by the fiber. This uncombined dyestuff could be washed off where yarn or cloth was in process, but fiber or loose cotton could not be dyed by this method, it being impracticable to remove the precipitation of color and mordant and render the fiber fit to carding and spinning. Therefore, the great bulk of the dyeing was done on yarn or cloth, but principally by hand. The repeated handling to obtain even distribution of the dyes and mordants and the wringing of the fiber to remove excess solutions caused such matting, tangling, and breakage as to interfere with the operations of spooling, sizing, and weaving, and caused many defects in the finished cloth. Indeed, the best practice and best equipment available at the time required more than forty-five handlings of the fiber. Yarn came out matted and harsh, and was frequently given four or more treatments through a neutral soap solution called a cotton softener. Naturally, every handling of the cotton caused some matting and roughing, some breakage, and considerable loss.

The advance that has been made in the dyeing of cotton in the last half-century has been due to improvements introduced by the chemist and contributions of the mechanical engineer.

Dyestuffs

Our readers are familiar with the fact that indigo is one of the oldest and is still the most extensively used dye. It is reasonably fast to washing and sunlight, and holds its blue shade even when badly faded. It was expected that indigo would be the first of the colors to have the serious attention of chemistry, and the story of its synthesis and the effect of Perkin's discovery of mauve upon organic chemical research has often been told. A number of the basic dyes were upon the market in the early eighties, and if they did

not provide all that could be desired as to fastness, they did offer a brilliancy that had not been dreamed of previously. Their production was profitable and the industry grew rapidly.

Following these basic dyes and alizarine came the substantive colors, which dye cotton without the intervention of a mordant so that it can be dyed in the raw stock or fiber as well as in the yarn or cloth. With this discovery there began the series of color changes that have affected the textile coloring industry.

The last twenty years have seen the introduction of derivatives of anthracene and thioindigo as vat colors. Rene Bohn, of the Badische Company, in endeavoring to make an anthraquinone analog of indigo, discovered the first of the anthraquinone vat colors and, in all-round fastness, they surpass anything which previously existed except Alizarine Red, although some of the members of the group are not so fast as others. Friedlander, by his scientific investigation of the sulphur analog of indigo, the sulphur replacing the imide group, discovered Thioindigo Red B, and that has given rise to a great many very good, very fast colors which can be applied easily and in fastness rank only second to the anthraquinone vat colors. This group is still in active process of development.

It seemed quite hopeless to find any azo colors which could compete with the fastness of the vat color series, but the dye chemist actually found such products in the ice colors made by padding the cotton fiber with the anilide of β-hydroxy naphthoic acid or its derivatives and developing with diazotized organic bases such as *m*-nitro-*p*-toluidine. The first success in this field in 1912 gave us reds comparable in fastness with Turkey Red and far easier to apply. Since then the group has been improved constantly and the range of color available is now quite striking, the fastness to light and to chlorine being comparable with that of the vat colors.

Fifty years carries us back to a period in which the dyeing of wool with chrome colors was comparatively undeveloped. The remarkable chrome blues and chrome blacks, which are now used in such large quantities that the wool dyer would be lost without them, are comparatively recent. For example, Diamand Black PV came on the market only twenty-three years ago; Diamond Black F in 1889.

All the dyestuffs used at present, with the exception of the basic colors, are inventions of the period we are commemorating. The first direct color was discovered only in 1884. The sulphur colors attained importance after 1900. The stilbene colors are covered by this period just as are the pyrazalone dyestuffs. Only those who are familiar with the dyestuff industry can appreciate what the chemist has done for the dyer, and therefore for the user of dyestuffs. The difference in brilliancy, in variety of shade, in cheapness of application, between the old dyestuffs of fifty years ago and those of the present day is indescribably great except to those intimately familiar with the art.

Dyeing Aids

One is apt to forget that some of the greatest triumphs of the chemist have been in the perfection of methods for the economic production of aids to dyeing. Under this head the most striking achievement has been that of producing dry sodium hyposulphite, which is an extremely readily oxidized material and one calling for great nicety in its preparation. In all civilized countries it has made the dyeing of indigo much simpler and actually the enormous spread of the use of vat colors has been possible only because of the commercial availability of sodium hyposulphite. In its modified form, condensed with formaldehyde, it acquires greater stability and has revolutionized the printing of cotton because it has enabled the printer to etch his ground—i. e., discharge it, as he says—instead of having to resist it which is a much less flexible method of printing. A still more stable form, basic zinc sulphoxylate formaldehyde, is used for stripping the color from shoddy, as it stands a boiling temperature and decomposes only slowly in an acid bath.

Very recently an organic form of chlorine has been placed at the disposal of the dyer, being a technical form of Chloramine T. As yet it is too early to state how valuable this will be.

In the phosphotungstic acids we have substances which not only precipitate basic colors as tannic acid does, but confer upon the lake a very remarkable fastness to light. This reagent has enabled us to use basic colors for tinting high-grade bond papers.

Recently, a great deal of attention has been given to the effect of the surface tension of the fiber, and a number of materials have been put on the market which serve to wet out the textile fiber. These materials, which come from all kinds of classes of organic compounds, are very effective and make package dyeing more certain. It would also seem that the most successful products in this class will enable the user of dyeing machines to cut down the time of his process because they will take the place, to some extent, of the very careful boil-out which is necessary before vat colors can be applied to give level results.

New mordants, new tanning agents, and materials for preventing damage to animal fiber by alkalies are also products of the immediate past.

Dye Formulas

The new dyes required a different mode of application and the old secret formulas were relegated to the past. In their stead the printed formula appeared with detail of all operations for the application of the new

(*Continued from page* 631)

Protein Compounds—III

The Combination of Proteins with Salts or Base-Protein-Acid Compounds—Halogen and Sulphur Compounds of Proteins—Abstracts from the Literature on Protein Compounds and Related Subjects.

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Base-Protein-Acid Compounds

WHILE some investigators, including Robertson, "The Physical Chemistry of Proteins," page 129, have suggested the formation of protein compounds with salts, such as for instance a base-protein-acid compound or according to Loeb's graphic formula, a compound corresponding to:

$$\begin{matrix} & -NH_2Cl \\ R & \\ & -COONa, \end{matrix}$$

neither Loeb nor Bogue, Chemical Technology of Gelatin and Glue, page 241, believe these compounds possible. Loeb's work upon the isoelectric point of gelatin and its compounds with acids and bases (either one alone, but not both), indicates that it is impossible to form a base-protein-acid compound, as the neutral protein is not ionized at its isoelectric point, as would be necessary for the formation of a protein compound. In the case of gelatin at pH 4.7 (its isoelectric point) he has shown that it is impossible for such a compound to form, while at a pH of more than pH 4.7, the protein unites with only the base and at less than pH 4.7 it combines only with the acid of the salt.

Atkin and Douglas, *J. Leather Trades Chem. 8*, 359-70 (1924), believe that such compounds may be possible at and near the isoelectric point and give neutralization curves to substantiate this belief. If the isoelectric "point" of an individual protein is really an isoelectric "range," then such compounds are highly probable, but only within this range. On the other hand, if our proteins, as we now know them, are really mixtures of closely related individual proteins, which appears highly probable, this apparent isoelectric range merely covers the range of the isoelectric points of the principal individual component proteins and again the base-protein-acid compounds of the individual component proteins become improbable. Within the isoelectric range, or range of minimal combination of the protein, some of the constituent proteins may be united with the cations present, while other component proteins may be united with the anions, according to which side of the isoelectric point the particular protein happens to be on.

Dr. Chapin's silver nitrate-wool-potassium ferrocyanide samples appear to indicate that wool has a rather definite isoelectric range, rather than a distinct isoelectric point. In view of the work of many investigators, including the recent work of Trotman, Trotman and Sutton,* which indicates that wool is composed of at least three distinct proteins, we might expect it to have such an isoelectric range rather than a definite point.

In spite of all this, Pfeiffer, *Z. angew. Chem. 36*, 137-8 (1923); *Z. Physiol. Chem. 133*, 22-61 (1924); and *143* 265-7 (1925); Pauli and Handovsky, *Biochem. Z. 18*, 340 (1909); *24*, 239 (1910); and Pauli and Wagner, *Biochem. Z. 27*, 296 (1910), and many others also contend that the amino acids and polypeptides form compounds with neutral salts. Pfeiffer states that he has prepared many such compounds with sodium, potassium, calcium, magnesium, barium, strontium, lithium, zinc, ammonia, etc.

Bugarszky and Liebermann, *Arch. ges. Physiol. 72*, 51 (1898), found that upon adding 6.4 grams of egg albumin to 100 c.c. of 0.05 *N* hydrochloric acid or sodium hydroxide, the difference between the freezing point of the solution and that of pure water is reduced nearly 50 per cent. Upon adding a similar quantity of the protein to a solution of sodium chloride, little or no alteration in the freezing point of the solution could be detected. This indicates, as mentioned in the previous paragraphs, that the proteins do not combine with the neutral salts.

They also found that while the addition of various proteins to acid or alkaline solutions caused a considerable difference in the amount of free ions in solution, by the concentration chain potentiometric method, the addition of the same protein to the solution of a neutral salt caused very little change in the electromotive force of the chain. This again indicates only a very slight change in the amount of protein in combination, as would be expected on the basis of the change in hydrogen ion concentration of the protein due to the presence of salt.

Hardy, *J. Physiol. 33*, 251 (1905), found only a slight (but what he considers an unmistakable) depression in the electrical conductivity of salt solutions upon saturation with serum globulin, and he believes that a very small amount of the base-protein-acid compound is formed, the amount of the compound formed varying with the quantity of salt present. Mellanby, *J. Physiol. 33*, 338 (1905), confirms Hardy's result as above. Very probably in all

*See American Dyestuff Reporter 15, 470 (1925).

such cases it is the hydrogen ion concentration, and its relations to the isoelectric point of the protein, which regulates the amount and character of the compound formed, and not the amount of salt present, directly.

Gustavson, *J. Amer. Leather Chem. Assoc. 21*, 206-16 (1926), in endeavoring to explain the antagonistic action of neutral salts on hide substance, brings in the secondary valency concept and bases his explanation on this. He believes that where the destructive action of neutral salts upon hide substance prevails, there is a tendency to the formation of neutral salt compounds similar to the glycine-calcium chloride compounds described by Pfeiffer (Org. Molekulverbindungen, Stuttgart, pages 106-24). The extent of the peptization depends upon the magnitude and stability of the secondary valency between the salt and protein micelles. A weakening and partial breaking up of the intermolecular forces occur by this combination and part of the hide is transformed into miscelles or complexes of molecular disperse order.

Just what the exact action of the neutral salts are on the proteins has not been definitely settled but certain of them appear to have considerable definite action. For instance, in medicine "normal" salt (sodium chloride) solution has long been used to cleanse the body membranes of mucous and other secretions which, of course, contain protein. It appears to increase the solubility of this material in some way. The action of sodium chloride and other neutral salts upon silk is well known to all textile chemists. This phase of the matter will be discussed more fully in connection with the action of reagents on wool.

The Halogen and Sulphur Compounds of Proteins

Hopkins, *Ber. chem. Ges. 30*, 1860 (1897); Hopkins and Brook, *J. Physiol. 22*, 184 (1897) Hopkins and Pinkus, *Ber. chem. Ges. 31*, 1311 (1898); and Blum and Vaubel, *J. prakt. Chem. 56*, 396 (1897); and *57*, 365 (1898), studied the bromine and chlorine substitution compounds of the proteins. They found that just as in the case of the chlorine compounds of wool, and the iodine compounds of certain other proteins, two kinds of bromine compounds exist (Robertson, "Physical Chemistry of the Proteins," page 158). In one of these compounds the percentage of bromine is small but is firmly bound. In the other, there is a larger percentage of bromine united in some way but a part of it is only loosely held. Hopkins and Brooks found 14.89 per cent of bromine in a brominated egg albumin of the latter type. Ostwald, *Z. physiol. Chem. 27*, 14 (1899); *32*, 121 (1901), found only 1.75 per cent of iodine in thyreoglobulin from the thyroid gland, and according to Mann, "Chemistry of the Proteids," London (1906), page 235, Hopkins and Blum found halogens in combination with egg albumin as given in Table XV:

TABLE XV

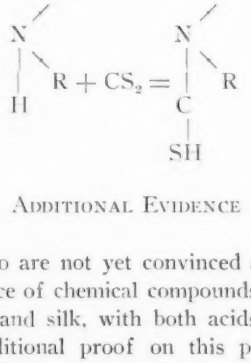
Percentage of Halogens in Combination with Egg Albumin

	Hopkins	Blum
Iodine	6.20	6 to 7
Bromine	2.84	4 to 5
Chlorine	1.93	4
Fluorine	....	1.2

According to Blum, *Z. physiol. Chem. 28*, 288 (1899); Blum and Vaubel, *J. prakt. Chem. 56*, 896 (1897); *57*, 365 (1898); Hofmeister, *Z. physiol. Chem. 24*, 159 (1898); Henze, *Z. physiol. Chem. 51*, 64 (1907); and Scott, *Biochem. Z. 1*, 4 (1906), the halogens form substitution compounds with the proteins by the replacement of hydrogen atoms in the aromatic groups by the halogen atoms, and they quote the naturally occurring and artificially prepared iodo-albumins as examples. Hopkins and Brook, *J. Physiol. 22*, 184 (1897), prepared these by the direct action of powdered iodine on the protein in solution.

An iodized keratin, gorgonin, is mentioned by Drechsel, *Z. Biol. 33*, 85 (1896); Henze, *Z. physiol. Chem. 38*, 60 (1903); Mendel, *Amer. J. Physiol. 4*, 243 (1900); and Morner, *Z. physiol. Chem. 51*, 33 (1907); *55*, 77 and 223 (1908), as occuring in corals. It contains about 8 per cent of iodine.

Uhl, *Z. prakt. Chem. 84*, 478 (1913), prepared sulphur compounds of the proteins by the action of carbon disulphide in alkaline solution according to:



Additional Evidence

For those who are not yet convinced as to the formation and existence of chemical compounds of the proteins, including wool and silk, with both acids and bases, and who desire additional proof on this point, the author can only refer them to the books already mentioned, the journal references quoted in the preceding papers, and those given in the following abstracts from the technical, medical, biological, and other scientific literature.

In addition to the books specifically mentioned previously should be added, "The Physical Chemistry of the Proteins," by T. Brailsford Robertson (1918, now out of print), who gives three chapters, pages 85 to 164, to this very important subject. Almost without exception, reference to the original papers covered by the following abstracts or references will give additional information on and proof of these chemical compounds which it is

impossible to include in the present papers due to lack of space. Further information along this line may also be obtained from the papers on the action of various reagents on wool, which will follow in later papers.

Graham, *Phil. Trans. Royal Soc. London 151,* 183 (1861), describes a compound of metaphosphoric acid with gelatin. Liebermann, *Ber. chem. Ges. 21,* 698 (1888); Malfatti, *Z. physiol. Chem. 16,* 69 (1892); Pohl. *Z. physiol. Chem. 13,* 292 (1889); and Kossel, *Arch. Physiol.* (1891) page 181, also studied these protein phosphoric acid compounds.

Hoppe-Seyler, *Med.-chem. Untersuch. Berlin* (1886) page 216; Osborne and Campbell, *Conn. Agri. Expt. Station Report No. 23* (1900); and Plimmer, *J. Chem. Soc. 93,* 1500 (1908), are inclined to believe that the proteins form compounds with lecithin, while Feinschmidt, *Biochem. Z. 38,* 244 (1912); and Alleman, *Biochem. Z. 45,* 346 (1912), have shown that the optimal isoelectric point of the proteins is influenced by the presence of lethicin.

Among the many renowned chemists who from time to time have advanced the chemical theory of protein reactions, perhaps the foremost in the textile field was the late Prof. E. Knecht, who in the *J. Soc. Dyers and Colourists 4,* 72-3 (1888) and many later papers, published considerable along this line in connection with dyeing. Prof. Knecht's papers will be considered in more detail in connection with dyeing theory.

Soldner, *Landwirthschaft. Veruchst. 35,* 351 (1888), stated that although uncombined casein is insoluble in water, the aqueous suspension acts as an acid in displacing carbon dioxide from carbonates and bicarbonates, forming a salt with the base.

Kossel, *Deutsch med. Wochenschr* (1894) No. 7; *Z. physiol. Chem. 31,* 188 (1900); and Kossel and Weiss, *Z. physiol. Chem. 49,* 308 (1906), have shown that the addition of the strongly basic protamines to a weakly alkaline solution of other proteins gives a precipitated compound resembling the natural histones. Hunter, *Z. physiol. Chem. 53,* 526 (1907), investigated these compounds and found that when digested with pepsin, the protamine is freed while the remainder of the compound is hydrolyzed. Gay and Robertson, *J. Expt. Med. 16,* 479 (1912); Robertson *J. Biol. Chem. 16,* 479 (1912); Robertson *J. Biol. Chem. 13,* 499 (1913); *Ugglas, Biochem. Z. 61,* (1914); *Schmidt, J. Biol. Chem. 25,* 63 (1916); and *Univ. Calif. Publ. Path. 2,* 157 (1916), also studied these compounds. Miescher, *Arch. Exper. Path. u. Pharm. 37,* 100 (1896), found that the protamines combine with chloroplatinic acid, and Goto. *Z. physiol. Chem. 37,* 94 (1902), investigated salmin chloroplatinate.

Bechamp, *Bull. Soc. Chem. (3) 11,* 153 (1894); and Salkowski, *Z. Biol. 37,* 404 (1899), investigated the ammonium compounds of the proteins.

Schlossman, *Z. physiol. Chem. 22,* 197 (1896); and Arny and Pratt, *Amer. J. Pharm. 78,* 121 (1906), describe compounds of the proteins with the alums.

Liebrecht, *Ber. chem. Ges. 30,* 1824 (1897), studied the iodine compounds of the proteins, and Ostwald, *Z. physiol. Chem. 95,* 351 (1915), gives details regarding their preparation.

Kossel, *Z. physiol. Chem. 25,* 165 (1898), presents evidence that the diamino and dicarboxylic acid radicals present in the proteins are active in the formation of compounds with acids or bases, respectively.

Mathews, *Amer. J. Physiol. 1,* 445 (1898), shows that lead acetate seldom precipitates proteins from a neutral solution, but readily precipitates them from an alkaline solution.

Osborne, *J. Amer. Chem. Soc. 21,* 486 (1899); *Z. physiol. Chem. 33,* 240 (1901); "The Vegetable Proteins," London (1909); and *Ergeb. physiol. 10,* 47 (1919), found that the inorganic acids combine with edestin, legumin, excelsin, amandin, corylin, phaseolin, gliadin, hordein and Zein.

Cohnheim and Krieger, *Z. f. Biol. 40,* 95 (1900), studied the acid combining power of the proteins, and Von Rhorer, *Arch. ges. Physiol. 90,* 368 (1902), continued this work.

Osborne, *J. Physiol. 27,* 398 (1901), has shown that when casein is titrated with calcium carbonate, a definite portion of the calcium is carried into solution in the form of a soluble calcium salt, with the evolution of carbon dioxide. In this way he prepared ammonium, potassium, sodium, lithium, magnesium, strontium and calcium caseinates.

Bechold, *Zeit. f. physiol. Chem. 34,* 122 (1901), describes compounds of egg albumin with orthophosphoric acid.

G. Mann, "Physiological Histology," Oxford (1902), gives a discussion of the chemical action of the dyestuffs used in staining tissues, etc.

Rohman and Hirschatein, *Beitr. chem. Physiol. und Path. 3,* 228 (1902), investigated the compounds of silver with casein and found that under certain conditions the amount of casein which reacts with the metal is directly proportional to the number of —COHN— groups which have been opened up by combination with a base. In other words, proportional to the hydrogen ion concentration. Galeotti, *Z. physiol. Chem. 42,* 330 (1904), found that silver united with egg albumin in molecular proportions, under the proper conditions.

Procter, "Principles of Leather Manufacture," London (1903), page 211, shows that chromium is only firmly united with hide substance when it is in the form of its cation Cr^{+++}. This union only occurs when the chromium salt is basic, or when the solution is neutral or alkaline.

Van Slyke and Hart, *Amer. Chem. J. 33,* 461 (1905); Bosworth and Van Slyke, *J. Biol. Chem. 14,* 207 (1913); Soldner, *Landwirthschaft. Versuchts. 35,* 351 (1888); and *Z. angew. Chem.* (1895), page 370; de Jager, *Neder,*

Tijdsche. Voor. Geneeskund. 2, 253 (1897); Laguer and Sackur, *Beitr. Z. chem. Physiol. u. Pathol 3*, 193 (1902); Courant, *Arch. Ges. Physiol. 50*, 109 (1891); and Timpe, *Arch. Hyg. 18*, 1 (1893), investigated the calcium compounds of casein.

Loevenhart, *Z. physiol. Chem. 41*, 177 (1904; and Van Slyke and Bosworth, *J. Biol. Chem. 14*, 211 (1913), investigated the calcium compounds of paracasein.

Van Slyke and Hart, *Amer. Chem. Jour. 33*, 451 (1905), found that on adding alcohol to a neutral (litmus) solution of calcium and casein, the precipitate contained exactly the same amount of calcium as that necessary to neutralize the casein to litmus. Similarly the precipitate from solutions neutrai to phenolphthalein contained the calculated amount of calcium.

Hardy, *J. Physiol. 33*, 251 (1905); *Robertson, J. Physiol. Chem. 11*, 437 and 542 (1907); *12*, 473 (1908); *14*, 528 and 601 (1901), found that on adding a protein to a highly ionized solution, the conductivity of the solution is diminished, and this change in conductivity is a measure of, but is not directly proportional to, the quantity of acid or base combined with the protein. *Sjoqvist, Arch. Physiol. 5*, 277 (1895), found that after a certain amount of protein is added to the solution, the molecular conductivity of the solution approaches constancy, indicating that all the acid is bound by the protein.

Osborne, *J. Physiol. 34*, 84 (1906) has shown that casein will form water soluble compounds with various alkaloids.

Suida, *Z. Physiol. Chem. 50*, 174 (1907); 68, 381 (1910), studied the compounds of various dyestuffs with the amino acids.

Robertson, *J. Physiol. Chem. 11*, 437 (1907); and *J. Biol. Chem. 5*, 155 (1908), studied the neutralization of acids and alkalies by globulin by means of potentiometric methods. He found that the acid equivalent of globulin rose with increasing acidity of the solution (hydrogen ion concentration).

Robertson, *J. Biol. Chem. 4*, 13 (1908), mentions some experiments upon the formation of protein-dyestuff compounds which appear to have been more or less overlooked by the textile chemists. He found that in some instances the water soluble protein compound of the dyestuff was insoluble in the organic solvents which dissolved the free dyestuff. In other cases insoluble protein dyestuff compounds were formed from soluble proteins and soluble dyestuffs. He also calls attention to the fact that some protein dyestuff compounds have a different color from that of the free color or its inorganic salts.

Rona and Michaelis, *Biochem. Z. 21*, 114 (1909), studied the compound or iron with casein. They found that the presence of proteins in aqueous soap solutions diminished the surface tension reducing power of the soap and they believe this to be due to the formation of a protein compound.

Berczeller, *Biochem. Z. 66*, 207 (1914), confirms the work of Rona and Michaelis regarding the surface tension of soap solutions in the presence of proteins.

Robertson, *J. Biol. Chem. 7*, 351 (1910), has shown that serum globulin is precipitated from serum by alcohol in the form of a compound with a base and not in the form of a free protein.

Pelet-Jolivet, "Die Theorie des Farbeprozesses," Dresden (1910), gives an interesting discussion of the reactions of dyestuffs with various proteins, etc.

Robertson, *J. Physiol. Chem. 14*, 709 (1910), investigated the compounds of ovomucoid with acids and bases by electrochemical methods.

Siegfried, *Ergeb. d. physiol. 9*, 334 (1910), describes a special form of combination between inorganic salts and amino- or poly-amino acids.

Erb, *Z. f. Biol. 41*, 309 (1910), using the method of Cohnheim and Kreiger, found that the amount of hydrochloric acid bound by the proteins varied with the concentration of the acid, which, of course, controls the hydrogen ion concentration of the protein, but arrived at some erroneous conclusions, as pointed out by Robertson, "Physical Chemistry of the Proteins," page 72.

Lippich, *Z. physiol. Chem. 74*, 360 (1911); *90*, 236 (1914), studied the zinc compounds of the proteins and believes that the compounds formed are controlled by a variety of factors, including the ionization, hydrolytic dissociation, etc.

Kober, *J. Biol. Chem. 10*, 9 (1911); Kober and Sugiura, *J. Biol. Chem. 13*, 1 (1912); *Amer. Chem. J. 48*, 383 (1912); and *J. Amer. Chem. Soc. 35*, 1546 (1913); and Osborne and Leavenworth, *J. Biol. Chem. 28*, 109 (1916), studied the copper compounds of the proteins, peptides, and amino acids.

Pauli and Falek, *Biochem. Z. 47*, 269 (1912), studied the effects of caffein upon the viscosity and conductivity of gelatin hydrochloride, and believes that a compound is formed.

Pauli, *Fortschr. naturwiss. Forschung 4*, 223 (1912), regards the combination of neutral salts with electrically neutral proteins as absorption compounds, while the reactions with acids and bases are true sale compounds.

M. Fort, *J. Soc. Dyers and Colourists 29*, 269-77 (1913); *31*, 80-3, 96-100, and 222-4 (1915), gives most excellent evidence of the formation of a chemical compound between the wool fiber and sulphuric acid, and finds that the mineral acid is displaced from its wool compound by the color of the acid in the acid dye bath. This work will be discussed fully in connection with the theory of dyeing wool.

Lloyd, *J. Soc. Dyers and Colourists 29*, 259-65 (1913), believes that silk reacts with sodium sulphate according to the equation:

$$\text{Silk} + 2H_2O + Na_2SO_4 = \text{Silk}.H_2SO_4 + \text{Silk}.2NaOH$$

Benedicenti, *Biochem. Z. 63*, 276 (1914), and Benedicenti and Revello-Alves, *Biochem. Z. 65*, 107 (1914), believe that the change in the magnetic properties of iron in a protein solution is due to compound formation.

Neuman, *Z. physiol. Chem. 89*, 149 (1914), studied

the compounds of zinc, copper, magnesium, aluminum, and iron with ovomucoid, and found that under similar conditions the amount of metal in combination was proportional to the molecular weight of the metallic hydroxide. That is, the hydroxides unite with proteins in stoichiometrical proportions.

Izar and Zuattro, *Biochem. Z. 59,* 226 (1914), prepared fatty acid compounds of the peptones by means of the fatty acid chlorides at low temperatures.

Procter, *J. Chem. Soc. 105,* 313-27 (1914), shows that the gelatin forms compounds with the various acids which ionize in the same manner as other salts of these acids.

Bosworth, *J. Biol. Chem. 20,* 91 (1915), studied the compounds of fibrin with acids and bases, and found that it unites with equivalent molecular proportions of different bases at the same hydrogen ion concentration.

Long and Hull, *J. Amer. Chem. Soc. 37,* 1593-1606 (1915), state that definite chemical compounds between the various proteins and the halogen acids can be obtained from mixtures of the protein with an excess of the acid, by evaporating over sulphuric acid at a low temperature, then over solid alkali, and finally drying at 75 deg Cent. These compounds contain much more acid than is suggested by titration, and the dry salts are extensively dissociated when mixed with water.

Osborne and Leavenworth, *J. Biol. Chem. 28,* 109 (1916), have shown that edestin will hold 34.67 per cent of its weight of cupric hydroxide in solution. This, on the basis of an atom of copper united to each atom of nitrogen, shows that ten out of every sixteen nitrogen atoms in the edestin molecule are in combination with the copper. It is more than a coincidence that this is exactly the proportion of nitrogen atoms in the edestin molecule that are present in the form of —COHN— groups; and that gliadin gives exactly similar results.

Wilson, *J. Amer. Leather Chem. Assoc. 12,* 108 (1917), suggests the possibility of interaction between the carboxyl radicals of protein with chromium cations in leather tanning. He also suggests the probable chemical mechanism of vegetable tannage to be the union between the amino groups of the protein and the tannic acid to form compounds such as substituted ammonium tannates. Thomas and Kelly, *Ind. and Eng. Chem. 15,* 1148 (1923), and *16,* 800 (1924), present evidence in favor of such a mechanism, while a study of the combining capacity of deaminized collagen for vegetable tannins by Thomas and Foster, *J. Amer. Chem. Soc. 48,* 489 (1926), apparently proves it. This latter study shows that the removal of amino nitrogen from hide protein resulted in a decrease in its tannin-combining capacity, just as the neutralizing power of gelatin toward hydrochloric acid is somewhat diminished when it is deaminized.

Most dyers are familiar with the process of resisting wool towards acid dyestuffs by means of a tannic acid treatment previous to dyeing. There appears to be many points in common between the resisting of wool by means of tannic acid, the lower chrome combining power of vegetable tanned leather, and the chemical theory of dyeing. However, more of this later.

Robertson, "Physical Chemistry of the Proteins" (1918), page 73, shows that if the alkali-binding capacity of casein were independent of the hydrogen ion concentration, the addition of any alkali beyond that necessary to carry the insoluble casein into solution would be without effect upon the number of equivalents of alkali neutralized by one gram of casein. As the hydroxyl ion concentration of the solution increases, however, the alkali-binding capacity of the casein, as determined by the potentiometric method, increases from 11.4 by 10^{-5} equivalents per gram to 180 by 10^{-3} equivalents per gram, or sixteen times the amount of alkali necessary to carry the casein into solution.

On page 85, R. says, "Examination of the modern literature, however, cannot fail to impress the reader with the conviction that in proportion to the adequacy of the chemical or physico-chemical technique employed, stoichiometrical relations between the proteins and the substances with which they combine are revealed or indicated."

He also points out that while the equivalents of acids or bases in combination with the protein varies with the hydrogen ion concentration of the protein, precisely analogous phenomena are met with among the complex and double salts, and the salts of polybasic acids or polyacid bases in organic chemistry. This, therefore, constitutes no legitimate grounds for the belief that the protein compounds are not molecular in character and consequently do not obey the law of constant combining proportions. He continues that, "All the accurate data we possess lend decided support to the view that although the proteins may enter into combination in multiple proportions, these proportions are constant and indicate that under definite conditions of reaction and concentration (hydrogen ion concentration) the protein molecules possess a definite and measurable equivalent weight."

J. Loeb, *Science 52,* 454 (1920), says that "the ratios in which the ions combine with proteins are identical with the ratios in which the same ions combine with crystalloids. Or, in other words, the forces by which gelatin and egg albumin (and probably all other proteins) combine with acids or alkalies are the purely chemical forces of primary valence." Also see J. Loeb, *J. Gen. Physiol. 3,* 85 (1920-1).

Trunkel, *Biochem. Z. 26,* 493 (1910), says, when so much of the published evidence on behalf of the "absorption theory" is of the unfortunate and inconclusive character, advocates of "adsorption" cannot complain if their hypotheses are viewed with skepticism by physical chemists.

A. Roncato, *Arch. sci. biol. 6,* 263-77 (1924), states that after shaking an egg albumin with powdered iron the ultra-violet spectrum is the same as that of albumin, showing that only an adsorption compound is formed. However, the addition of a trace of ionized iron produces

an essential change, indicating the formation of a true chemical compound.

Schofield, "Wet Processes of the Wool Industry" (1924), pages 39-42, after a careful review of the literature on the action of acids on wool, writes, "The problem of the reactions of wool or rather keratin, with acids, alkalies and chemical reagents generally, should be considered in the light of the general protein reactions of similar type. Erroneous conclusions have undoubtedly been drawn, owing to an unduly narrow outlook in such researches. In the case of sulphuric acid, a mere absorptive view of the reaction appears to have been the prevailing standpoint, almost exclusive of the possibility of chemical combination. Yet in other proteins such combination is indisputable. Hence the controversy regarding the permanent retention of acids, etc., by wool has been largely one-sided." "The balance of evidence appears to be that keratin or wool substances forms real compounds with acids."

In "Recent Advances in Protein Chemistry," H. B. Vickey, *Ind. and Eng. Chem. 16*, 1029 (1924), very aptly says that salt formation in the strictest sense of the term, with all the qualitative and quantitative implications, is entirely adequate to explain the behavior of proteins with small concentrations of acids and alkalies. With larger concentrations nothing is known which is incompatible with this view, although under extreme conditions unexplained irreversible changes occur which result in the so-called "denaturing" of the protein. In recent years we have learned, therefore, to look upon proteins, not as mysterious colloidal complexes, but as chemical individuals of, in certain cases, quite well-known composition, with properties which conform to the laws of classical chemistry."

He continues that it should be pointed out, however, that proteins can and often do occur in colloidal form. The colloidal chemists have quite rightly claimed certain of the properties of these substances for their field; but they have often been misled by a lack of the appreciation of the capacity of the proteins to enter into true chemical combination with other substances. Moreover, the difficulties encountered by many are readily explained by a lack of purity of their protein preparations. Chemists have frequently carried out elaborate research with purified reagents and highly accurate physical apparatus upon grossly impure material. . . . Chemists have every reason for gratification at the remarkable achievements in the field of protein chemistry in recent years. A much clearer comprehension of the problems has been attained, and the ground is well prepared for future research, which will undoubtedly yield results of the greatest importance.

In a paper on "Proteins as Chemical Compounds," *J. Soc. Chem. Ind. 43*, 144 (1924), before the Yorkshire Section of the Society of Chemical Industry, Atkin and Douglas state that in consequence of the work of Procter and Wilson, and Loeb, proteins are no longer regarded simply as "colloids" and the peculiarities in their behavior towards acid and alkalies hitherto "explained" by adsorption and other vague terms as gradually being eliminated. In truth, the solubility in acid and alkali is due to chemical combination. Quoting Procter, they state that gelatin forms salts with acids capable of ionizing and variations in swelling are correlated with osmotic pressure effects. Loeb demonstrated their amphoteric character with an isoelectric point at pH 4.7. The titration results of Harris and Hopkins with lysine, with the corrections introduced, show clearly how their curve for lysine was made up of two neutralization curves, and in their examination of gelatin it behaved in a similar manner.

They continue that carefully purified gelatin, which does not set to a jelly but is gradually precipitated, was made up to 1 per cent solution and titrated with acid and alkali at 25 deg. Cent., using a hydrogen electrode and correcting for hydrolytic effects. The gelatin was neutralized by hydrochloric acid at pH 3.65, corresponding to a combined weight of 1,100, and by sodium hydroxide at pH 5.65, combining weight 3,000. Further, after pH 7, there is evidence that soda is being attached; in other words, the gelatin is behaving like a weak polybasic acid. These results were shown to be in agreement with calculations made from the results of Dakin's work on the nature of the gelatin molecule.

W. F. Hoffman and R. A. Gortner, *Second Colloid Symposium Monograph*, 1925, 209-368, report investigations on a number of proteins, and found that by potentiometric methods the same weight of protein, irrespective of chemical composition, bound approximately the same amount of acid or alkali when the final pH was more than 2.5 or less than 10.5. The log of the acid or alkali equivalents bound gave straight lines when plotted against the logs of equivalents of acid or alkali added, or against the final pH as abscissas. Compared on a normality basis, a unit amount of protein bound approximately equivalent amounts to hydrochloric, sulphuric or phosphoric acid. They contradict Loeb's statement regarding the amounts of hydrochloric and phosphoric combined at equivalent pH, and state that much more phosphoric is bound than hydrochloric acid.

Plotting the logs of equivalents of acid or alkali bound against those of acid or alkali added, the lines for a single protein passed through a common point; for acids this was approximately pH 2.5, and for alkalies approximately pH 10.5. Between these limits, the amount of acid or alkali bound apparently depends on the chemical composition of the protein. The logs of equivalents of acid and alkali bound in this pH region do not give straight lines when plotted against logs of final pH. "It is suggested that there are two types of combinations between proteins and acid or alkali: (1) a chemical type of combination which takes place between the hydrogen ion concentration represented by pH 2.5 and 10.5, and (2) an adsorption type of combination which takes place when the hydrogen-ion concentration is greater than pH 2.5 or the hydroxyl-ion concentration is greater than

pH 10.5." "The analytical data in regard to the amino acid content of the prolamines glaidins are not sufficiently accurate to enable final conclusions to be drawn as to the chemical groups responsible for the chemical binding of alkali. In the case of acid binding, however, a correlation of r = 0.9923 ± 0.00275 was found between the free amino nitrogen of the protein as determined in the Van Slyke apparatus, and the equivalents of acid bound at pH 2.8, and a correlation of 0.9918 ± 0.00312 was obtained between the sum of the free amino nitrogen plus one-fourth of the arginine nitrogen (free amino group of the guanidine nucleus) and the equivalents of acid bound at pH 2.5." On calculating the isoelectric points by extrapolating the log curves of type two, the acid and alkali curves intersect near pH 7. This was so whether the isoelectric point was calculated from (1) logs of the amount of acid and alkali bound and logs of their original concentration, (2) amounts of acid and alkali bound and equivalent pH, (3) logs of amount of acid and alkali added and equivalent pH. The potentiometrically determined pH of the protein suspended in water does not, in a number of instances agree with these extrapolated values, but is in the neighborhood of the values determined directly by cataphoresis and other methods as given in the literature. The isoelectric "point" is probably an isoelectric "range," the position of the range on the off scale being dependent on the chemical composition of the protein. "The calculated isoelectric point is very near the isoelectric point of neutral water. This is what would be predicted on the theory that at higher concentrations of acid and alkali, the binding of acid and alkali follows the adsorption law. The calculated isoelectric points are not related to the chemical composition of the protein."

Gorton and Hoffman, *Science 62*, 464-7 (1925), write that the chemical nature of a protein and the power of the protein to bind acid or alkali in stoichiometrical relationships depend on the chemical groups within the protein molecule, and is limited to the range between pH 2.5 and pH 10.5. They suggest that there are two types of combinations between proteins and acid or alkali; (1) a chemical type as above indicated and (2) an adsorption type of combination which takes place at pH values outside the limits 2.5 to 10.5.

K. H. Gustavson and P. J. Wilson, *Ind. and Eng. Chem. 17*, 577-83 (1925), in reporting upon the reactions between chrome liquors and hide substance conclude that "The data from this investigation cannot be based upon the concept of the combination of chrome and hide substance as being an adsorption only involving physical forces, but form, instead, an additional link in the chain of evidence demonstrating the justification of extending the ionic concept to reactions of proteins."

According to I. M. Kolthoff, *Chem. Weekblad 22*, 489-94 (1925), the proteins are chemical individuals, ampholytes with individual minimum equivalent weights with respect to H^+ and OH^-, the free carboxyl and amino groups being responsible for the acid and alkali binding capacity. He points out the difficulties by which the absorption theory is faced and its failure to explain the mechanism of the reactions with alkalies and acids and the influence on these reactions of polyvalent ions with opposite charge.

According to E. Stiasny, *Gerber. 51*, 163-7, 173-6 (1925), pure polypeptides react with acids only through their amino groups and with alkalies only through their carboxyl groups at less than pH 10.5, but at higher pH values the peptide linkage also reacts with alkali.

A. Ponte in the *J. Soc. Leather Trades Chem. 9*, 336-99 (1925), reports the results of some experimental work upon the retention of various acids by delimed calf pelt. These were immersed in 1.0 *N*, 0.1 *N*, and 0.1 per cent solutions of sulphuric, hydrochloric, formic, acetic, tartaric and citric acids for fifteen hours, washed by immersion for thirty minutes in twelve changes of alcohol, twelve changes of water, and twenty-four changes of water respectively. The amount of acid taken up by the hide was greatest with the 1.0 *N* solutions and after washing with alcohol, each wash removing further portions of the acid. Comparison of the results for the different acids, expressed in terms of hydrochloric acid, shows that the amount of acid remaining in the pelt depends on the nature and chemical activity of the acid, its basicity, and to a smaller degree, on the concentration of the solutions used. In explaining the fact that a larger amount of polybasic acid is fixed than of a monobasic acid, it is assumed that the hide substance, $R(NH_2)_2$, combines with acids to form salts of the types $R(NH_2)_2.2HCl$, and $R(NH_2)_2.H_2SO_4$, which are hydrolyzed on washing to compounds of the types $(NH_3OH)RNH_3.HCl$ and $(NH_3OH)RNH_3(SO_4H)$.

Shukoff and Stschoukareff, *J. Physical Chem. 29*, 285-94 (1925), state that by following the titration of hydrochloric acid by sodium hydroxide in the presence of commercial gelatin with a hydrogen electrode, it was found that the titration curves met at a point corresponding to pH 5.6. They assume that this curve is due to the fact that gelatin is a mixture of two substances with different isoelectric points. The decrease in the amount of sodium hydroxide required to be added to the solutions in order to produce a given pH value between 3.5 and 5.6 is proportional to the amount of gelatin in solution. Similarly the increase in sodium hydroxide required to produce a given pH value between 5.6 and 10.5 is also proportional to the amount of gelatin present. Hence, for a definite pH value, the number of hydrogen or hydroxyl ions bound by a gram of gelatin is constant and independent of the concentration of the gelatin.

In a recent investigation upon the behavior of deaminized collagen, Thomas and Foster, *J. Amer. Chem. Soc. 48*, 489-501 (1926), give the following evidence in favor of the chemical nature of tanning. Treatment of animal skin with nitrous acid yields a product of diminished nitrogen content. The isoelectric point of such "deaminized collagen" is in the region of pH 3.5 to 4, as revealed by the dye technique and other methods, while that of

the original protein was about pH 5; see Thomas and Kelly, *J. Amer. Soc. 44*, 195 (1922). From a purely chemical point of view, the more acid character of "deaminized collagen," in comparison with collagen, is to be expected upon removal of nitrogenous groups. If the combination between skin and organic tannins is fundamentally a chemical reaction between nitrogenous groups of the protein molecule and the acidic tannins, then collagen which has been impoverished in its nitrogen groups should show a diminished rate of tanning in acid solutions and a shift in the minimum rate to a more acid region. Thomas and Foster found this to be true in their experiments.

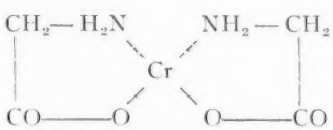
J. A. Wilson, *Ind. and Eng. Chem. 18*, 47-50 (1926), states that when acid enters into chemical combination with leather, it actually ceases to be acid, even though so indicated by the method of analysis employed. Also, "these experiments show that the large amount of acid normally found by analysis in chrome leather is not present as free acid; on the contrary, the great sensitivity of chrome leather to destruction by acid indicates that only a very small amount of the acid of chrome leather is present in the free state. However, the acid found in chrome leather is capable of neutralization, and as fast as the small amount of free acid is removed more is liberated to take its place. Chrome leather may be looked upon as a sulphuric acid reservoir having a high capacity factor and a low intensity factor." "The apparently much lower capacity of vegetable-tanned leather for acid seems to be due to the tannins combining with the protein groups which are otherwise capable of combining with acid. Wilson and Pear (not yet published) have found that an increasing degree of vegetable-tannage renders hide substance less capable of removing acid from solution. They have also found that the sulphuric acid content of chrome tanned leather is decreased materially by vegetable retanning."

In discussing the chemistry of tanning, K. H. Gustavson, *J. Amer. Leather Chem. Assoc. 21*, 53-7 (1926), states that chrome tanning cannot be explained as absorption, which is a meaningless term in this connection. The absorption conception cannot explain why the combination of hide substance and chromium in a 50 per cent basic liquor exhibits a sharp maximum at 17.5 grams of chromic oxide per liter, why this maximum shifts to a lower concentration with increasing basicity, why two further points of maximum occur under certain conditions, and why sulphates and chlorides behave very differently.

E. Wolesensky in "Behavior of Synthetic Tanning Materials Toward Hide Substance," Tech. Paper of the Bureau of Standards, No. 309 (1926), says, "The tanning process, in the case of the type A syntans (synthetic tanning materials), appears to be a true chemical combination of the tanning material through its sulphonic acid groups with the hide substance, probably through amino groups of the hide protein, while in the case of the type B syntans, in addition to this chemical combination, the tanning process appears to include also some other mode of fixation, possibly adsorption."

K. H. Gustavson, *J. Amer. Leather Chem. Assoc. 21*, 22-30 (1926), writes that with decrease in the percentage acidity of chrome liquors, there is an increased fixation of chrome by formaldehyde-collagen and for a moderately acid salt this increase is accentuated by increasing concentration of the liquor. The grass-green color of the tanned formaldehyde compound seems to show that the color of ordinary chrome-tanned leather is due to internal salt formation between the secondary valencies of the chromium salts and the basic groups of the proteins. Fixation of chromium containing anions is decreased by pretreatment of the collagen with formaldehyde. Hide powder tanned with sumac, quebracho, and tannic acid at pH 2.0 to 6.0 shows decreased fixation of chromium from chromium chlorides and sulphates (up to 50 per cent reduction). In concentrated basic liquors part of the tannin is replaced by chromium, probably due to the fixation of electro-negative sulphato-complexes. The oxalato-compound showed a proportionately lesser retardation in the chromium fixation by the tannin-collagen compounds than the salts in which chromium is present as cation.

He points out that the degree of chromium fixation by hide substance from ordinary chrome liquors is determined not only by the state of the acidic groups, but is also a function of the basic groups of the protein. Hide powder tanned by means of chromium cations shows no decreased affinity for vegetable tannins. Hide powder tanned with oxalato-chromium compounds shows a slight decrease in the rate of vegetable tanning. The reactivity of deaminied collagen and tannin-collagen compounds towards cathodic and anodic chromium is similar and this resemblance supports the inner complex hypothesis of chrome tanning, according to which the chrome-collagen compound is an internal complex salt of the type:



The primary valency is probably concerned in the reaction of chromium salts with the acidic groups in collagen (and keratin) and secondary valency with the basic groups. Anodic chromium fixation from the oxalato-compounds shows a maximum rate in the isoelectric zone of the proteins and is probably of the residual valency type. This reaction is distinctly different from the combination of chormium cations with collagen.

In regards to the formation of chemical compounds in tanning leather, Thomas and Foster, *J. Amer. Chem. Soc. 48*, 489-501 (1926), state that from a purely chemical point of view, the more acid character of "deaminized collagen" in comparison with collagen is to be expected upon the removal of nitrogen groups. If the combination between skin and organic tannins is fundamentally a

chemical reaction between the nitrogen groups of the protein molecule and the acidic tannins, then collagen which has been impoverished in its nitrogen groups should show a diminished rate of tanning in acid solutions and a shift in the minimum rate to a more acid region. This has been found to be true.

A. T. King, *Dyer and Calico Printer 55*, 34-6 (1926), states that wool appears to consist of a variety of amino acids in some form of combination, and that it to some degree possesses the properties of these amino acids. As these acids are amphoteric, they form salts with both acids and bases, and while both the acid and basic properties of the amino acids are feeble, the salt formed with either sulphuric acid or sodium hydroxide is comparatively stable. "Wool behaves similarly, but with this difference, that whereas with the amino acids the acid groups, and the amino or basic groups, are free to react easily; in the case of wool, these groups must be regarded as fettered or chained up, and their activity subdued. In other words, wool if not actually amphoteric, is at least pontentially so. Thus wool combines with sulphuric acid, for example, forming a salt which we may term keratin sulphate, and with sodium hydroxide forming sodium keratinate." . . . "Some chemists prefer to regard this taking up of acid and alkali by wool as a purely physical absorption. I have not time to review the evidence on this point,, which to my mind is conclusively in favor of the chemical standpoint."

Last, but certainly not least, the well known fact may be mentioned that wool is dyed by a larger number of dyestuffs, of a wider variety, and to a greater fastness, than any other natural fiber. In other words, it appears to be more reactive than its nearest relation, silk, or any other fiber. Silk follows it as a close second in this respect and takes up the dyes at a lower temperature than does wool. It is possible that this slight difference in the reactivities of wool and silk proteins with dyes may be due to the differernces in their physical structure, inasmuch as wool is cellular but amorphous, while silk is not cellular but contains a crystalline constituent.*

That this dyeing reaction is chemical in nature, and not physical, is demonstrated by the fact that upon immersing wool in a hot colorless solution of rosaniline base, the fiber is dyed red just as though rosaniline hydrochloride had been applied instead of the colorless base. It is well known that the rosaniline base alone will not dye, and that the color is formed by the union of the colorless base with an acid. In this case the amphoteric protein wool acts as the acid, forming the colored compound.

(*This is the eighth paper of the series on "Wool" by Mr. Mullen. The next paper will deal with some general reactions of the keratins and the related proteins. It will appear in an early issue.*)

*See "The Constitution of Wool," American Dyestuff Reporter 15, 468-9 (1926).

STANDARD CELLULOSE NEEDED

Absence of progress in the technology of vegetable fibers and the importance of a standard cellulose in studies of that nature are given brief mention by the German correspondent of Industrial and Engineering Chemistry. He says: "In spite of the great progress in the textile industry, in spite of the astonishing development of artificial silk manufacture, in spite of the discovery of various new fibers, the scientific investigation of vegetable fibers is not really progressing. Many contradictions still keep occurring in the literature. These are ascribed by Prof. Carl G. Schwalbe, the well-known cellulose investigator, to the fact that raw material of differing age has been used. As far back as 1913 Schwalbe demanded that a so-called standard cotton cellulose be made available to research workers, as is already the case in America. But this standard cellulose must be designated precisely, as to the year of production and duration of storage; furthermore, in addition, along with a standard cotton cellulose, a definite standard wool cellulose, and if possible definite flax and hemp varieties must be made available. However, it must be borne in mind in their use, that even these standard celluloses undergo a continual alteration, which can only be offset by most careful storage, if possible with the aid of preservatives."

REPORT OF THE DYE DIVISION, AMERICAN CHEMICAL SOCIETY

The general dye papers of the A. C. S. Dye Division meeting were given on Tuesday morning, September 7, and among these was a paper continuing the work of Gordon and White on absorption of dyes by gels. This was followed by a number of excellent contributions from the chemists of the Color Laboratory involving a process of making alizarine from o-dichlorobenzene and phthalic anhydride using aluminum chloride by Phillips, and the determination of the vapor pressures at varying temperatures of the toluidines, naphthols and nitro-toluenes by Berliner, May and Lynch. The abstracts of these papers appeared in the last issue of The Reporter.

At the business meeting of the division the following officers were elected for the ensuing year:

Chairman, M. L. Crossley, of Calco Chemical Company; vice-chairman, E. K. Bolton, of Du Pont Company; secretary-treasurer, H. T. Herrick, of Color Laboratory. Additional members of the Executive Committee, C. H. Herty and C. G. Derick.

Following the regular program was a Symposium on "The Progress of Dye Industry in the United States During the Past Decade," which was arranged by Dr. Crossley. This was a supplement to the previous symposium held several years ago describing the prior war accomplishments in the dye field. The abstracts of these papers have also been published.

Foreign Dyes Imported Through New York and Other Ports During August

Compiled by the Chemical Division of the Bureau of Foreign and Domestic Commerce in Collaboration with the Chemical Division of the United States Tariff Commission

KEY TO ABBREVIATIONS OF MANUFACTURERS' NAMES

1—THE SIX LEADING GERMAN COMPANIES

A—Actien-Gesellschaft fur Anilin-Fabrikation, Berlin. Founded 1873.
B—Badische Anilin-und-Soda-Fabrik, Ludwigshafen-on-the-Rhine. Founded 1865.
By—Farbenfabriken, vormals Friedr. Bayer & Co., Leverkusen-on-the-Rhine. Founded 1862.
C—Leopold Cassella & Co., Frankfort-on-the-Main. Founded 1870.
K—Kalle & Co., A. G., Biebrich-on-the-Rhine. Founded 1870.
M—Farbwerke, vormals Meister Lucius & Bruning, Hochst-on-the Main. Founded 1862.

2—THE SMALLER GERMAN COMPANIES

BK—Leipziger Anilinfabrik Boyer & Kegel, Furstenberg, near Leipzig. Founded 1882.
CG—Chemikaliewerk Griesheim G. m. b. H., Griesheim-on-the-Main. Founded 1882.
CJ—Carl Jager G. m. b. H., Anilinfarbenfabrik, Dusseldo-f. Founded 1823
GrE—Chemische Fabrik Griesheim-Electron, Offenbach-on-the-Main. Founded 1842.
L—Farbwerk Mulheim, vormals A. Leonhardt & Co., Mulheim-on-the-Main. Founded 1879
tM—Chemische Fabriken, vormals Weiler ter Meer, Uerdingen-on-the-Rhine. Founded 1877.
WD—Wulfing, Dahl & Co., A. G. Barmen. Founded 1842.

3—SWISS COMPANIES (ALL AT BASEL)

DH—Farbwerke vormals L. Durand, Huguenin & Co. Founded 1871.
G—Anilinfarben-und Extract-Fabriken, vormals Joh. Rud. Geigy. Founded 1764.
I—Gesellschaft fur chemische Industrie. Founded 1885.
S—Chemische Fabrik, vormals Sandoz & Co. Founded 1887

4—DUTCH AND FRENCH COMPANIES

FA—Farbwerk Ammersfoort, Ammersfoort, Netherlands. Founded 1888
NF—Niederlandische Farben-und-Chemikalienfabrik Delft, Delft, Netherlands. Founded 1897.
CN—Compagnie Nationale de Matieres Colorantes et Produits Chimiques. Founded 1917. (Etablissements Kuhlmann merged with this company in 1923.)
P—Societe Anonyme des Matieres Colorantes et Produits Chimiques St. Denis (formerly A. Poirrier). Founded 1830.

5—ENGLISH COMPANIES

Bro—Brotherton & Co., Ltd., City Chambers, Leeds.
BAC—British Alizarine Co., Ltd., Manchester
BD—British Dyestuffs Corporation, Ltd., London.
Cl Co.—The Clayton Aniline Co., Ltd., Clayton, Manchester.
CV—The Colne Vale Dye & Chemical Co., Ltd., Milnsbridge, Huddersfield.
Hol—L. B. Holliday & Co., Ltd., Huddersfield.
Scot—Scottish Dyes, Ltd., Grangemouth.

FOREIGN coal-tar dyes imported through New York and other ports during the month of August totaled 380,414 pounds, with an invoice value of $298,159. Imports by ports were as follows: New York, 371,336 pounds, with an invoice value of $289,868; Albany, 8,143 pounds, with an invoice value of $7,908; Boston, 920 pounds, with an invoice value of $668, and Detroit, 15 pounds, valued at $15.

Imports of Synthetic Dyes

	1926		1925	
	Pounds	Invoice Value	Pounds	Invoice Value
January	190,459	$184,018	403,984	$359,376
February ..	479,027	477,255	373,259	365,268
March	487,804	435,891	527,964	488,501
April	437,526	401,606	451,005	426,141
May	392,739	343,745	370,271	347,904
June	333,319	317,896	376,668	333,654
August	380,414	298,159	330,674	303,612
Total 3,052,713		$2,761,649	3,509,668	$3,317,071

Five Leading Dyes, by Quantity, Imported During August, 1926

	Pounds
Cibanone Yellow R (single strength).....	32,182
Rhodamine B (single strength).....	24,165
Indanthrene Yellow G (single strength).....	17,544
Indanthrene Blue GCD (single strength)....	11,998
Helindone Printing Black RD Paste.....	10,000

Dyes and Intermediates Remaining in Bonded Customs Warehouse

	Coal-Tar Dyes and Colors (pounds)	Coal-Tar Intermediates (pounds)
January 31, 1926.....	703,159	763,409
February 28, 1926.....	596,154	855,170
March 31, 1926.....	447,588	896,530
April 30, 1926.....	359,164	928,593
May 31, 1926.....	535,226	946,120
June 30, 1926.....	671,396	772,475
July 31, 1926.....	212,186	781,796

Per Cent of Dyes by Country of Shipment

	1926			
	Aug.	July	June	May
Germany	47.0	60.0	51.5	60.0
Switzerland	34.0	30.0	36.0	28.0
France	2.5	2.7	1.0	1.0
England	0.5	1.4	7.5	3.0
Belgium	5.5	4.0	3.0	5.5
Canada	8.5	—	0.5	0.5
Italy	2.0	1.5	0.5	1.0
Holland	—	—	—	1.0
All others	—	0.4	—	—

The dyes in this report are grouped by both Colour Index and Schultz numbers, and, in the case of those which could not be identified by either number, the classification according to the ordinary method of application was adopted. As the pastes and powders of the vat dyes vary widely in strength and quantity, each vat dye has been reduced—in nearly every case—to a single-strength basis.

DYES OF COAL-TAR ORIGIN

Colour Index No.	Schultz No.	Name of Dye and Mfr.	Quantity (pounds)
35	48	Metachrome Yellow RA—(IG)	2
40	58	Chrome Orange R—(DH)	110
169	156	Ortho Cerise B—(IG)	2
278	—	Benzo Fast Red 8BL—(IG)	400
288	256	Sulphon Cyanine G—(IG)	2,000
316	273	Blue NA—(IG)	167
319	—	Benzo Fast Heliotrope BL—(By) Benzo Fast Heliotrope 2RL—(By)	1,500
325	—	Brilliant Benzo Violet B—(By)	1,156
345	296	Cotton Yellow G Extra—(IG)	300
349	—	Chlorantine Fast Yellow 4GL—(I)	661
372	319	Chloramine Red B—(S) Chloramine Red 3B—(S)	6,007
388	—	Benzo Violet R—(IG)	25
409	339	Diamine Orange B—(IG)	500
436	358	Chloramine Red 8BS—(By)	330
441	—	Chromocitronine R—(DH)	441
449	364	Diazo Brilliant Black B—(IG)	500
487	400	Acid Milling Red R Conc.—(G) Brilliant Milling Red R—(IG)	1,402
488	404	Diamine Yellow N Powder—(IG)	100
559	448	Diamine Bronze G—(IG)	25
561	449	Trisulphon Brown B Conc.—(S)	2,000
591	472	Chloramine Blue HW—(S)	2,000
596	476	Benzo Chrome Brown G—(IG)	50
628	206	Diphenyl Catechine G Supra—(G)	4,409
639	22	Supra Light Yellow 2GL—(By)	2,335
658	496	Rhoduline Blue 6G—(IG) Setoglaucine—(G)	951
653	496	Setocyanine—(G)	110
666	502	Guinea Green B—(IG)	2
667	503	Benzyl Green B—(I) Brilliant Acid Green 6B—(By) Guinea Fast Green 3B—(IG) Prosciden Green SGX—(IG)	1,736
670	505	Acid Green Conc.—(M)	15
671	506	Kiton Blue L—(I)	2,205
677	512	Magenta AB—(IG)	2,000
681	516	Crystal Violet C Conc.—(G)	110
682	518	Ethyl Violet—(B)	400
699	531	Eriocyanine AC—(G)	1,102
707	539	Water Blue—(AG)	200
712	543	Brilliant Acid Blue V—(By) Patent Blue V—(IG)	3,000
714	545	Kiton Blue A—(I)	551
715	546	Blue Extra—(C) Blue FF—(C)	477
720	551	Eriochrome Azurol BC—(G)	2,205
724	555	Aurine—(Lo)	336
728	558	Victoria Blue R—(I)	220
729	559	Basic Pure Blue BO—(B)	591
735	564	Alkali Fast Green 3G—(IG)	1,987
748	579	Sulpho Rhodamine B—(M)	76
749	573	Rhodamine B Conc. (s. s.)—(G) Rhodamine B Extra (s. s.)—(B) Rhodamine B Extra (s. s.)—(I) Rhodamine B Extra (s. s.)—(IG)	24,165
751	574	Rhodamine 3B Extra (s. s.)—(IG)	125
757	580	Fast Acid Violet B—(IG)	300
758	582	Fast Acid Violet R—(IG)	100
789	—	Brilliant Phosphine 5G—(I) Patent Phosphine G—(I)	992
795	607	Runic AL Conc.—(IG)	200
797	608	Euchrysine RRDX—(B) Patent Phosphine GRNTN—(IG)	2,060
828	672	Azo Carmine GX—(B) Azo Carmine GX—(IG)	1,857
829	673	Azocarmine BX—(IG) Rosinduline 2B Bluish—(K)	683
833	—	Benzyl Fast Blue BL—(I) Zylene Milling Blue GL Conc.—(S)	2,057
875	923	Fur Blue Black A—(IG) Fur Blue Black SB—(IG) Fur Gray G—(IG)	725
876	620	Capri Blue GON Conc.—(IG)	50
879	—	Chromazurine G Powder—(DH)	441
899	640	Modern Azurine 5G—(DH)	11
924	660	Methylene Green G Extra—(S) Methylene Green W—(G)	4,528
926	661	Thionine Blue GO—(IG)	500
971	748	Hydron Blue B Powder (s. s.)—(IG)	667
1027	778	Alizarine Red VI Extra Pure—(IG)	4,410
1034	780	Alizarine Red S Powder—(IG) Alizarine Red W Powder—(By)	684
1039	785	Alizarine Red XGP Paste—(By)	1,602
1053	—	Alizarine Light Blue SE Conc.—(S) Alizarine Sapphire Blue SE—(I)	1,284
1054	858	Alizarine Light Blue B—(S) Alizarine Sapphire Blue B—(I)	5,572
1064	—	Alizarine Cyclamine R Paste—(IG)	798
1067	804	Alizarine Blue S Powder—(IG)	2,000
1073	852	Alizarine Irisol R Powder—(IG) Alizarine Blue JR—(By)	1,461
1077	860	Alizarine Direct Blue BGAOO—(IG)	1,000
1078	865	Alizarine Cyanine Green G—(By) Alizarine Cyanine Green 3G—(IG)	894
1082	863	Anthraquinone Blue Green BXO—(IG)	150
1084	854	Alizarine Viridine FF—(DH)	1,102
1088	855	Alizarine Sky Blue B Powder—(By)	1,652
1091	—	Alizarine Rubine GW Powder—(By) Alizarine Rubine R Powder—(By)	991
1093	850	Vat Blue WB Powder—(B)	342

Colour Index No.	Schultz No.	Name of Dye and Mfr.	Quantity (pounds)
1095	759	Anthra Yellow GC Powder (s. s.)—(B)	808
1096	760	Vat Golden Orange G Double Paste (s. s.) —(IG)	
		Vat Orange G Double Paste Fine (s. s.) —(IG)	9,902
1097	761	Vat Orange RRT Paste Fine (s. s.)—(IG)	4,857
1099	763	Vat Dark Blue BOA Pst. Fine (s .s.)—(IG)	2,505
1104	767	Vat Brilliant Violet RR Paste Fine—(B)	
		Vat Brilliant Violet RR Powder (s. s.)—(B)	3,385
1106	838	Vat Blue RSP Triple Powder (s. s.)—(IG)	1,500
1109	840	Vat Blue 3G Powder (s. s.)—(IG)	
		Vat Blue 3G Paste (s. s.)—(IG)	2,500
1113	842	Cibanone Blue GCD Dbl. Pst. (s. s.)—(I)	
		Indan. Blue GCD Dbl. Pst. (s. s.)—(B)	
		Vat Blue GCD Dbl. Pst. Fine (s. s.)—(M)	11,998
1118	849	Sandothrene Yellow NG—(S)	
		Vat Yellow G Dbl. Pst. s. s.)—(IG)	
		Vat Yellow G Dbl. Pst. Fine (s. s.)—(IG)	
		Vat Yellow G Powder (s. s.)—(B)	
		Vat Yellow G Powder (s. s.)—(IB)	17,544
1133	819	Algol Red R Extra Paste—(By)	
		Algol Red R Extra Powder (s. s.)—(IG)	2,797
1143	827	Anthra Bordeaux B Paste—(IG)	466
1145	834	Vat Gray GK Paste—(By)	
		Vat Gray GK Powder (s. s.)—(IG)	2,264
1149	873	Vat Brown GR Paste—(IG)	500
1150	833	Vat Olive R Powder (s. s.)—(IG)	3,200
1151	—	Vat Brown IR Powder (s. s.)—(M)	
		Vat Brown R Paste—(By)	2103
1152	—	Vat Brown B Paste—(GrE)	
		Vat Brown G Paste—(By)	
		Vat Brown G Paste—(IG)	
		Vat Brown G Powder (s. s.)—(IG)	4,628
1155	825	Algol Red B Paste—(By)	400
1161	871	Indan. Reddish Violet RRK (s. s.)—(B)	8
1163	832	Vat Violet BN Paste Fine—(B)	2,300
1170	795	Cibanone Yellow R Paste—(I)	
		Cibanone Yellow R Powder (s. s.)—(I)	32,182
1173	793	Cibanone Blue 3G Paste—(I)	2,204
1188	884	Brilliant Indigo BB Paste—(IG)	2,505
1207	912	Anthra Red B Paste—(IG)	1,034
1212	918	Ciba Red 3B Powder (s. s.)—(I)	
		Thioindigo Red 3B Powder (s. s.)—(K)	
		Vat Red Violet RH Paste—(IG)	
		Vat Red Violet RH Powder (s. s.)—(IG)	9,910
1217	913	Helindone Orange R Powder (s. s.)—(IG)	
		Vat Orange R Powder (s. s.)—(M)	2,560
1228	907	Thioindigo Scarlet 2G Paste—(IG)	1,500
1229	908	Ciba Red R Paste—(I)	9,038

UNIDENTIFIED DYES

Acid Dyes

Name of Dye and Manufacturer	Quantity (pounds)
Acid Milling Yellow G Conc.—(S)	500
Acid Red RS Conc.—(Q)	222
Alizarine Brilliant Sky Blue R—(IG)	25
Alizarine Supra Blue A—(IG)	1,400
Alkali Fast Green 2BF—(By)	100
Astra Violet FF Extra—(IG)	100
Brilliant Acid Blue FF—(By)	220
Brilliant Bordeaux S—(IG)	2
Brilliant Milling Blue B—(C)	1,543
Brilliant Scarlet N—(IG)	500
Brilliant Wool Blue FFB Extra—(IG)	100
Brilliant Wool Blue FFR Extra—(IG)	500
Cloth Fast Red 3B—(I)	110
Cloth Fast Yellow G—(I)	495
Fast Acid Green BB Extra—(I)	500
Fast Light Red B—(By)	200
Guinea Blue A4B—(IG)	2
Guinea Blue V4B—(IG)	2
Guinea Brown 2GX—(IG)	2
Guinea Carmine B—(IG)	2
Indo Violet BF—(IG)	2
Indocyanine B—(A)	1,544
Ink Blue BITBN Powder—(IG)	1,000
Kiton Fast Red 4BL—(I)	1,764
Kiton Fast Red GL—(I)	110
Milling Yellow H3G—(IG)	20
Milling Yellow O—(IG)	1,500
Milling Yellow R—(IG)	2
Neolan Blue B—(I)	661
Neolan Blue G—(I)	551
Neolan Blue GG—(I)	1,102
Novazol Blue B—(G)	551
Onis 3B, 5B—(IG)	1,100
Pilatus Fast Blue B—(IG)	100
Pilatus Fast Blue GG—(IG)	200
Pilatus Fast Gray B—(IG)	100
Pilatus Fast Green BL Conc.—(IG)	25
Pilatus Fast Pink B—(IG)	200
Pilatus Fast Pink G—(IG)	50
Pilatus Fast Violet R—(IG)	100
Pilatus Fast Yellow G—(IG)	200
Polar Yellow 2G Conc.—(G)	882
Radio Yellow R—(IG)	500
Suiphon Orange G—(By)	572
Supramine Red B—(IG)	1,000
Wool Blue R Extra—(IG)	200
Wool Fast Yellow R Powder—(By)	441

Vat Dyes

Name of Dye and Manufacturer	Quantity (pounds)
AlizarineAlizarine Indigo 5R Paste—(IG)	500
Anth a Scarlet B Paste—(IG)	
Anth a Scarlet B Powder (s. s.)—(IG)	1,700
Ciba Blue 2RH—(I)	110
Ciba Pink BG Powder (s. s.)—(I)	1,100
Cibanone Orange 6R Powder—(I)	110
Eridan Brilliant Scarlet B Paste—(IG)	500
Helindone Printing Black RD Paste—(IG)	10,000
Hydron Blue BBF Paste—(IG)	100
Hydron Brown G Powder (s. s.)—(C)	
Hydron Brown R Paste—(C)	793
Hydron Orange GL Paste—(IG)	286
Hydron Scarlet 3B Powder (s. s.)—(C)	354
Hydron Scarlet 3B Paste—(C)	1,445
Hydron Violet RF Paste—(IG)	100
Hydron Yellow GG Powder (s. s.)—(IG)	600
Indanthrene Brown RT Paste—(By)	397
Indigosol O4B—(DH)	
Indigosol O4B—(By)	310
Indigosol Black TB—(IG)	100
Indigosol Orange HR—(DH)	55
Indigosol Pink HR—(DH)	55
Indigosol Violet A2B—(IG)	200
Vat Black B Paste for Printing—(K)	673
Vat Blue GK Powder—(IG)	50
Vat Brilliant Blue R Powder (s. s.)—(IG)	800
Vat Brown GG Powder (s. s.)—(IG)	
Vat Brown GG Paste—(B)	1,713
Vat Golden Yellow GK Double Paste (s. s.)—(IG)	1,000
Vat Green GG Double Paste (s. s.)—(B)	

Name of Dye and Manufacturer	Quantity (pounds)
Vat Green GG Double Paste (s. s.)—(IG)	1,872
Vat Gray 3B Double Paste (s. s.)—(IG)	956
Vat Orange 3R Paste Fine—(B)	1,764
Vat Orange 6RTK Paste—(IG)	
Vat Orange 6RTK Powder (s. s.)—(IG)	450
Vat Printing Brown R Paste—(IG)	2,152
Vat Printing Red B Paste—(IG)	500
Vat Red BK Paste Fine—(IG)	100

Mordant and Chrome Dyes

Acid Alizarine Gray G—(IG)	
Acid Alizarine Gray G—(M)	1,429
Acid Anthracene Red 3BL—(By)	200
Acid Chrome Red B—(IG)	25
Alizarine Blue Green BBS Conc.—(S)	1,000
Alizarine Light Gray BBS Conc.—(S)	2,996
Brilliant Chrome Blue S—(DH)	110
Brilliant Chrome Violet 3RA—(DH)	441
Chrome Fast Green G—(IG)	2
Chromorhodine 6GN Extra—(DH)	110
Chromoxane Brilliant Violet SB—(By)	1,000
Eriochromal Brown G Powder—(G)	110
Eriochrome Geranol R—(G)	992
Eriochrome Red G—(G)	551
Metachrome Blue Black 2BX—(A)	826
Metachrome Brown BL—(IG)	2
Metachrome Brown 6G—(IG)	2
Metachrome Olive B—(IG)	2
Metachrome Orange R—(IG)	100
Metachrome Red G—(IG)	200
Modern Blue CVI—(DH)	220
Naphthochrome Violet R—(I)	551
New Gallophenine 5G—(IG)	50
Omega Chrome Brown EB—(S)	200
Oxychrome Brilliant Blue PB—(A)	300
Radiochrome Blue B—(IG)	1,000

Direct Dyes

Benzo Chrome Black B—(IG)	25
Benzo Chrome Brown 5G—(IG)	100
Benzo Fast Brown 3GL—(IG)	1,000
Benzo Chrome Brown RL—(IG)	450
Benzo Fast Gray BL—(IG)	1,000
Benzo Fast Heliotrope 5RH—(By)	55
Benzo Fast Light Scarlet 4BL—(IG)	200
Benzo Fast Orange 2RL—(By)	500
Benzo Fast Yellow RL—(IG)	500
Benzo Red 12B Powder—(By)	132
Benzo Rhoduline Red B, 3B—(IG)	400
Brilliant Benzo Fast Yellow GL—(IG)	300
Brilliant Congo Blue 5R—(A)	200
Brilliant Benzo Violet R—(IG)	300
Brilliant Sky Blue 8G Extra—(By)	973
Brilliant Sky Blue R—(By)	200
Chlorantine Fast Blue 2GL—(I)	2,205
Chlorantine Fast Blue 8GL—(I)	2,204
Chlorantine Fast Brown 3RL—(I)	2,205
Chlorantine Fast Gray B—(I)	1,543
Chlorantine Fast Orange 2RL—(I)	220
Chlorantine Fast Violet 5BL—(I)	2,204
Chlorantine Fast Violet RL—(I)	2,204
Chlorantine Fast Violet 2RL—(I)	1,102
Chlorantine Fast Yellow 4GL—(I)	441
Cotonerol A Extra—(IG)	500
Cotton Black AC—(IG)	100
Developing Black ED—(IG)	125
Diamine Azo Brown 3G—(C)	505
Diamine Azo Fast Violet R—(C)	265
Diamine Azo Green G—(C)	440
Diamine Catechine G—(IG)	100
Diamine Fast Orange EG—(IG)	500
Diamine Fast Orange ER—(IG)	1,000
Diamine Gray G—(IG)	100
Diamineral Blue BF—(IG)	500
Diaminogene Blue GG—(C)	551
Dianil Fast Violet BL—(IG)	300
Diazo Bordeaux 7B—(By)	661
Diazo Brilliant Green 3G—(By)	
Diazo Brilliant Green 3G—(IG)	2,200
Diazo Brilliant Scarlet 2BL—(By)	441
Diazo Brown 3R—(IG)	50
Diazo Fast Bordeaux BL—(IG)	993
Diazo Fast Green GF—(IG)	600
Diazo Fast Violet BL—(By)	500
Diazo Green 3G—(IG)	100
Diazo Indigo Blue 2RL—(IG)	1,000
Diazo Pure Blue B Powder—(By)	1,323
Diazo Rubine B—(By)	400
Diazol Light Red N8B—(StD)	2,204
Direct Cutch Brown GR—(I)	1,653
Fast Cotton Gray VL—(IG)	500
Half Wool Blue 3R—(IG)	500
Minaxo Light Pink BBX—(IG)	200
Parasulphon Brown G—(S)	500
Rosanthrene R—(I)	661
Rosanthrene Orange R—(I)	551

Dyes for Artificial Silk

Artificial Silk Black R—(IG)	500
Artisil Carmine B Conc.—(S)	100
Artisil Purple Conc.—(S)	100
Duranol Blue G Paste—(BD)	112
Ionamine Red KA—(BD)	60
Setacyl Direct Blue G Powder—(G)	220

Rapid Fast Dyes

Rapid Fast Pink LB Paste—(IG)	200

Basic Dyes

Basic Pink G Powder—(Q)	110
Brilliant Rhodamine Blue R—(Q)	226
Methyl Violet 4B—(IG)	200
Rhodamine 6GDN Extra (s. s.)—(IG)	5,000

Sulphur Dyes

Immedial Brown W Conc.—(IG)	1,000
Indocarbon CL—(IG)	200
Pyrogene Cutch 2R Extra—(I)	1,102
Thionol Yellow GR—(BD)	465

A LIST OF APPRAISEMENTS OF COAL-TAR PRODUCTS WITHIN PARS. 27 AND 28 OF THE TARIFF ACT OF 1922

The following supplemental list contains the month of entry, the name of the product within paragraphs 27 and 28, together with the designations as "C" (for competitive) and "NC" (for non-competitive), which indicates the appraisement basis for the assessment of the ad valorem duty in paragraphs 27 and 28 of the Tariff Act of 1922.

The ad valorem rate for competitive dyes is based on the

Colour Index No.	Schultz No.	Name of Dye and Mfr.	Quantity (pounds)
1095	759	Anthra Yellow GC Powder (s. s.)—(B)	808
1096	760	Vat Golden Orange G Double Paste (s. s.) —(IG)	
		Vat Orange G Double Paste Fine (s. s.) —(IG)	9,902
1097	761	Vat Orange RRT Paste Fine (s. s.)—(IG)	4,857
1099	763	Vat Dark Blue BOA Pst. Fine (s .s.)—(IG)	2,505
1104	767	Vat Brilliant Violet RR Paste Fine—(B)	
		Vat Brilliant Violet RR Powder (s. s.)—(B)	3,385
1106	838	Vat Blue RSP Triple Powder (s. s.)—(IG)	1,500
1109	840	Vat Blue 3G Powder (s. s.)—(IG)	
		Vat Blue 3G Paste (s. s.)—(IG)	2,500
1113	842	Cibanone Blue GCD Dbl. Pst. (s. s.)—(I)	
		Indan. Blue GCD Dbl. Pst. (s. s.)—(B)	
		Vat Blue GCD Dbl. Pst. Fine (s. s.)—(M)	11,998
1118	849	Sandothrene Yellow NG—(S)	
		Vat Yellow G Dbl. Pst. s. s.)—(IG)	
		Vat Yellow G Dbl. Pst. Fine (s. s.)—(IG)	
		Vat Yellow G Powder (s. s.)—(B)	
		Vat Yellow G Powder (s. s.)—(IB)	17,544
1133	819	Algol Red R Extra Paste—(By)	
		Algol Red R Extra Powder (s. s.)—(IG)	2,797
1143	827	Anthra Bordeaux B Paste—(IG)	466
1145	834	Vat Gray GK Paste—(By)	
		Vat Gray GK Powder (s. s.)—(IG)	2,264
1149	873	Vat Brown GR Paste—(IG)	500
1150	833	Vat Olive R Powder (s. s.)—(IG)	3,206
1151	—	Vat Brown IR Powder (s. s.)—(M)	
		Vat Brown R Paste—(By)	2 103
1152	—	Vat Brown B Paste—(GrE)	
		Vat Brown G Paste—(By)	
		Vat Brown G Paste—(IG)	
		Vat Brown G Powder (s. s.)—(IG)	4,628
1155	825	Algol Red B Paste—(By)	40,
1161	871	Indan. Reddish Violet RRK (s. s.)—(B)	8
1163	832	Vat Violet BN Paste Fine—(B)	2,390
1170	795	Cibanone Yellow R Paste—(I)	
		Cibanone Yellow R Powder (s. s.)—(I)	32,182
1173	793	Cibanone Blue 3G Paste—(I)	2,204
1188	884	Brilliant Indigo BB Paste—(IG)	2,505
1207	912	Anthra Red B Paste—(IG)	1,034
1212	918	Ciba Red 3B Powder (s. s.)—(I)	
		Thioindigo Red 3B Powder (s. s.)—(K)	
		Vat Red Violet RH Paste—(IG)	
		Vat Red Violet RH Powder (s. s.)—(IG)	9,910
1217	913	Helindone Orange R Powder (s. s.)—(IG)	
		Vat Orange R Powder (s. s.)—(M)	2,560
1228	907	Thioindigo Scarlet 2G Paste—(IG)	1,500
1229	908	Ciba Red R Paste—(I)	9,038

UNIDENTIFIED DYES

Acid Dyes

Name of Dye and Manufacturer	Quantity (pounds)
Acid Milling Yellow G Conc.—(S)	500
Acid Red RS Conc.—(Q)	222
Alizarine Brilliant Sky Blue R—(IG)	25
Alizarine Supra Blue A—(IG)	1,400
Alkali Fast Green 2BF—(By)	100
Astra Violet FF Extra—(IG)	100
Brilliant Acid Blue FF—(By)	220
Brilliant Bordeaux S—(IG)	2
Brilliant Milling Blue B—(C)	1,543
Brilliant Scarlet N—(IG)	500
Brilliant Wool Blue FFB Extra—(IG)	100
Brilliant Wool Blue FFR Extra—(IG)	500
Cloth Fast Red 3B—(I)	110
Cloth Fast Yellow G—(I)	495
Fast Acid Green BB Extra—(I)	500
Fast Light Red B—(By)	200
Guinea Blue A4B—(IG)	2
Guinea Blue V4B—(IG)	2
Guinea Brown 2GX—(IG)	2
Guinea Carmine B—(IG)	2
Indo Violet BF—(IG)	2
Indocyanine B—(A)	1,544
Ink Blue BITBN Powder—(IG)	1,000
Kiton Fast Red 4BL—(I)	1,764
Kiton Fast Red GL—(I)	110
Milling Yellow H3G—(IG)	20
Milling Yellow O—(IG)	1,500
Milling Yellow R—(IG)	2
Neolan Blue B—(I)	661
Neolan Blue G—(I)	551
Neolan Blue GG—(I)	1,102
Novazol Blue B—(G)	551
Onis 3B, 5B—(IG)	1,100
Pilatus Fast Blue B—(IG)	100
Pilatus Fast Blue GG—(IG)	200
Pilatus Fast Gray B—(IG)	100
Pilatus Fast Green BL Conc.—(IG)	25
Pilatus Fast Pink B—(IG)	200
Pilatus Fast Pink G—(IG)	50
Pilatus Fast Violet R—(IG)	100
Pilatus Fast Yellow G—(IG)	200
Polar Yellow 2G Conc.—(G)	882
Radio Yellow R—(IG)	500
Suiphon Orange G—(By)	572
Supramine Red B—(IG)	1,000
Wool Blue R Extra—(IG)	200
Wool Fast Yellow R Powder—(By)	441

Vat Dyes

AlizarineAlizarine Indigo 5R Paste—(IG)	500
Anth a Scarlet B Paste—(IG)	
Anth a Scarlet B Powder (s. s.)—(IG)	1,700
Ciba Blue 2RH—(I)	110
Ciba Pink BG Powder (s. s.)—(I)	1,100
Cibanone Orange 6R Powder—(I)	110
Eridan Brilliant Scarlet B Paste—(IG)	500
Helindone Printing Black RD Paste—(IG)	10,000
Hydron Blue BBF Paste—(IG)	100
Hydron Brown G Powder (s. s.)—(C)	
Hydron Brown R Paste—(C)	795
Hydron Orange GL Paste—(IG)	286
Hydron Scarlet 3B Powder (s. s.)—(C)	354
Hydron Scarlet 3B Paste—(C)	1,445
Hydron Violet RF Paste—(IG)	100
Hydron Yellow GG Powder (s. s.)—(IG)	600
Indanthrene Brown RT Paste—(By)	397
Indigosol O4B—(DH)	
Indigosol O4B—(By)	310
Indigosol Black TB—(IG)	100
Indigosol Orange HR—(DH)	55
Indigosol Pink HR—(DH)	55
Indigosol Violet A2B—(IG)	200
Vat Black B Paste for Printing—(K)	673
Vat Blue GK Powder—(IG)	50
Vat Brilliant Blue R Powder (s. s.)—(IG)	800
Vat Brown GG Powder (s. s.)—(IG)	
Vat Brown GG Paste—(B)	1,713
Vat Golden Yellow GK Double Paste (s. s.)—(IG)	1,000
Vat Green GG Double Paste (s. s.)—(B)	

Name of Dye and Manufacturer	Quantity (pounds)
Vat Green GG Double Paste (s. s.)—(IG)	1,872
Vat Gray 3B Double Paste (s. s.)—(IG)	956
Vat Orange 3R Paste Fine—(B)	1,764
Vat Orange 6RTK Paste—(IG)	
Vat Orange 6RTK Powder (s. s.)—(IG)	450
Vat Printing Brown R Paste—(IG)	2,152
Vat Printing Red B Paste—(IG)	500
Vat Red BK Paste Fine—(IG)	100

Mordant and Chrome Dyes

Acid Alizarine Gray G—(IG)	
Acid Alizarine Gray G—(M)	1,429
Acid Anthracene Red 3BL—(By)	200
Acid Chrome Red B—(IG)	25
Alizarine Blue Green BBS Conc.—(S)	1,000
Alizarine Light Gray BBS Conc.—(S)	2,996
Brilliant Chrome Blue S—(DH)	110
Brilliant Chrome Violet 3RA—(DH)	441
Chrome Fast Green G—(IG)	2
Chromorhodine 6GN Extra—(DH)	110
Chromoxane Brilliant Violet SB—(By)	1,000
Eriochromal Brown G Powder—(G)	110
Eriochrome Geranol R—(G)	992
Eriochrome Red G—(G)	551
Metachrome Blue Black 2BX—(A)	826
Metachrome Brown BL—(IG)	2
Metachrome Brown 6G—(IG)	2
Metachrome Olive B—(IG)	2
Metachrome Orange R—(IG)	100
Metachrome Red G—(IG)	200
Modern Blue CVI—(DH)	220
Naphthochrome Violet R—(I)	551
New Gallophenine 5G—(IG)	50
Omega Chrome Brown EB—(S)	200
Oxychrome Brilliant Blue PB—(A)	300
Radiochrome Blue B—(IG)	1,000

Direct Dyes

Benzo Chrome Black B—(IG)	25
Benzo Chrome Brown 5G—(IG)	100
Benzo Fast Brown 3GL—(IG)	1,000
Benzo Chrome Brown RL—(IG)	450
Benzo Fast Gray BL—(IG)	1,000
Benzo Fast Heliotrope 5RH—(By)	55
Benzo Fast Light Scarlet 4BL—(IG)	200
Benzo Fast Orange 2RL—(By)	500
Benzo Fast Yellow RL—(IG)	500
Benzo Red 12B Powder—(By)	132
Benzo Rhoduline Red B, 3B—(IG)	400
Brilliant Benzo Fast Yellow GL—(IG)	300
Brilliant Congo Blue 5R—(A)	200
Brilliant Benzo Violet R—(IG)	300
Brilliant Sky Blue 8G Extra—(By)	973
Brilliant Sky Blue R—(By)	200
Chlorantine Fast Blue 2GL—(I)	2,205
Chlorantine Fast Blue 8GL—(I)	2,204
Chlorantine Fast Brown 3RL—(I)	2,205
Chlorantine Fast Gray B—(I)	1,543
Chlorantine Fast Orange 2RL—(I)	220
Chlorantine Fast Violet 5BL—(I)	2,204
Chlorantine Fast Violet RL—(I)	2,204
Chlorantine Fast Violet 2RL—(I)	1,102
Chlorantine Fast Yellow 4GL—(I)	441
Cotonerol A Extra—(IG)	500
Cotton Black AC—(IG)	100
Developing Black ED—(IG)	125
Diamine Azo Brown 3G—(C)	505
Diamine Azo Fast Violet R—(C)	265
Diamine Azo Green G—(C)	440
Diamine Catechine G—(IG)	100
Diamine Fast Orange EG—(IG)	500
Diamine Fast Orange ER—(IG)	1,000
Diamine Gray G—(IG)	100
Diamineral Blue BF—(IG)	500
Diaminogene Blue GG—(C)	551
Dianil Fast Violet BL—(IG)	300
Diazo Bordeaux 7B—(By)	661
Diazo Brilliant Green 3G—(By)	
Diazo Brilliant Green 3G—(IG)	2,200
Diazo Brilliant Scarlet 2BL—(By)	441
Diazo Brown 3R—(IG)	50
Diazo Fast Bordeaux BL—(IG)	993
Diazo Fast Green GF—(IG)	600
Diazo Fast Violet BL—(By)	500
Diazo Green 3G—(IG)	100
Diazo Indigo Blue 2RL—(IG)	1,000
Diazo Pure Blue B Powder—(By)	1,323
Diazo Rubine B—(By)	400
Diazol Light Red N8B—(StD)	2,204
Direct Cutch Brown GR—(I)	1,653
Fast Cotton Gray VL—(IG)	500
Half Wool Blue 3R—(IG)	500
Minaxo Light Pink BBX—(IG)	200
Parasulphon Brown G—(S)	500
Rosanthrene R—(I)	661
Rosanthrene Orange R—(I)	551

Dyes for Artificial Silk

Artificial Silk Black R—(IG)	500
Artisil Carmine B Conc.—(S)	100
Artisil Purple Conc.—(S)	100
Duranol Blue G Paste—(BD)	112
Ionamine Red KA—(BD)	60
Setacyl Direct Blue G Powder—(G)	220

Rapid Fast Dyes

Rapid Fast Pink LB Paste—(IG)	200

Basic Dyes

Basic Pink G Powder—(Q)	110
Brilliant Rhodamine Blue R—(Q)	226
Methyl Violet 4B—(IG)	200
Rhodamine 6GDN Extra (s. s.)—(IG)	5,000

Sulphur Dyes

Immedial Brown W Conc.—(IG)	1,000
Indocarbon CL—(IG)	200
Pyrogene Cutch 2R Extra—(I)	1,102
Thionol Yellow GR—(BD)	465

A LIST OF APPRAISEMENTS OF COAL-TAR PRODUCTS WITHIN PARS. 27 AND 28 OF THE TARIFF ACT OF 1922

The following supplemental list contains the month of entry, the name of the product within paragraphs 27 and 28, together with the designations as "C" (for competitive) and "NC" (for non-competitive), which indicates the appraisement basis for the assessment of the ad valorem duty in paragraphs 27 and 28 of the Tariff Act of 1922.

The ad valorem rate for competitive dyes is based on the

American selling price as defined in Subdivision (f) of Section 402 of Title IV; the ad valorem rate for non-competitive dyes is based on the United States value as defined in Subdivision (d) of Section 402 of Title IV of the Tariff Act of 1922.

This list contains the appraisements received since the publication of the July list for the Port of New York, beginning with January, 1926.

JANUARY

Acid Pure Blue R Supra 614	NC
Alizarine Cyanine Green Extra Powder	C
Anthra Pink B Extra Paste	C
Anthra Red RT Paste	NC
Anthra Red RT Paste Fine	NC
Anthra Red RT Double Paste Fine	NC
Anthracene Blue SWR Powder	NC
Benzo Fast Blue 4GL	C
Benzo Fast Gray BL	NC
Brilliant Acid Blue EG	NC
Brilliant Wool Blue FFR Extra	NC
Cotton Red 4BX	C
Diazo Brilliant Blue 2BL Extra	NC
Diazo Indigo Blue 4GL Extra	NC
Diazo Sky Blue 3GL	NC
Direct Gray R Paste 1022	NC
Erio Green B Supra 657	C
Eriochrome Flavine A Conc. 1015	C
Ethyl Violet	NC
Gallamine Blue Extra Paste 900	NC
Garnet Red BB Paste	NC
Madder Lake 75 Powder	C
Magenta Powder AB	C
Methyl Silk Blue New 706	NC
New Fast Gray	NC
Novazol Blue B966	NC
Patent Phosphine GRNTN New	C
Polar Orange R Conc. 599	NC
Polar Yellow 2G Conc. 602	NC
Runic AL Conc	NC
Setocyanine 396	NC
Stone Fast Yellow GN Lumps	NC
Sulphon Yellow 5G	NC
Tero Yellow FR	NC
Vat Blue RSN Powder	C
Vat Pink B Paste	NC
Erio Anthracene Brown R888	NC
Erio Cyanine CR	C

FEBRUARY

Aceto Purpurine 8B	NC
Hydron Scarlet 3B Powder	NC
Vat Green G Powder	NC
Vat Orange R Paste	C
Vat Red BN Extra Paste	NC
Vat Red Violet RH Paste	NC

MARCH

Acid Blue RBF	NC
Acid Ponceaux E640	NC
Alizarine Blue AS Powder	NC
Anthra Pink BN Paste	NC
Anthra Yellow GC Powder	NC
Azo Carmine GX	NC
Chloramine Red 8BS	NC
Chlorantine Fast Blue 2GL	C
Chlorantine Fast Bordeaux 2BL	NC
Chlorantine Red 8BN	NC
Chrome Azurol S Conc. 1004	NC
Chrome Violet 905	NC
Ciba Red 3B Paste	NC
Ciba Red R Paste	NC
Ciba Yellow G Paste	NC
Cibanone Brown R Powder	NC
Cloth Fast Red 3B	NC
Cyanol Extra	NC
Delta Purpurine 5B Powder	C
Diazo Brown RW	NC
Diphenyl Brown GS	C
Direct Cutch Brown GR	C
Erio Green B Supra	C
Erio Viridine B Supra 561	C
Eriochrome Blue S	NC
Eriochrome Flavine A Conc. 1105	C
Erioglaucine EP	NC
Gallamine Blue Extra Paste 900	NC
Indocyanine B	NC
Kiton Fast Yellow 3G	C
Methyl Silk Blue New 706	NC
Pyrogene Pure Blue 3GL	NC
Rhodamine B Extra	C
Thio Indigo Red 3B Paste	NC
Trisulphon Bronze BG	NC
Vat Red RK Paste	NC
Vat Violet BN Paste	NC

APRIL

Alkali Fast Green 3G	C
Chlorantine Fast Violet 5BL	NC
Chlorantine Fast Violet 2RL	NC
Chlorantine Red 8BN	NC
Chrome Azurol B	NC
Ciba Yellow G Paste	NC
Cibanon eBlack B Paste New	NC
Cibanone Orange 6R Powder	C
Danubia Blue BX	NC
Diazo Fast Black SD	C
Indanthrene Blue GCD Double Paste	C
Kiton Blue L	C
Kiton Fast Green A	NC
Kiton Fast Green V	C
Madder Lake 71 Extra Powder	C
Onis 5B	NC
Quinolene Yellow	C
Supramine Red 2G	NC
Vat Gray 3B Double Paste	NC
Victoria Blue B	C

MAY

Auramine G	NC
Brilliant Acid Blue G	NC
Chloramine Light Gray B Conc	NC
Chloramine Red B	C
Chloramine Red 8BS	NC
Chlorantine Fast Green B	NC
Chlorantine Fast Red 7BL	C
Chlorantine Fast Yellow 4GL	C
Chlorantine Red 8BN	NC
Ciba Yellow G Paste	NC
Cibanone Orange R Paste	NC
Cibanone Orange 6R Powder	C
Cibanone Red G Powder	NC
Diaminogene Blue NA	C
Diazo Red N8B	C
Indigosol Orange HR	NC
Indigosol Pink HR Extra	NC
Kiton Blue A	C
Kiton Fast Red 4BL	NC
Kiton Fast Yellow 3G	NC

Neolan Black RR	NC
Neolan Blue B	NC
Neolan Blue BR	NC
Neolan Blue GR	NC
Vat Red RK Paste	C
Xylene Fast Blue FF Conc	NC

JUNE

Alizarine Light Blue B	C
Alizarine Light Blue SE Conc	C
Alizarine Rubine GW Powder	C
Alizarine Rubine R Powder	C
Brilliant Acridine Orange 3R	NC
Chloramine Brilliant Red 8B Conc	NC
Chromacetine Blue S Extra	NC
Chromazurine DN	NC
Ciba Pink BG Powder	NC
Ciba Red 3B Powder	NC
Ciba Scarlet G Extra Paste	NC
Eriochrome Red G978	NC
Eriochrome Yellow G Paste 946	C
Fast Cyanine Blue B	NC
Fast Cyanine Violet B	NC
Formal Fast Black G Conc. 280	NC
Gallazine No. 90	NC
Indochromine RR Conc	NC
Methylene Blue Pure 0.1 gm	NC
Modern Gray CVX	NC
Modern Violet	NC
Neolan Blue G	NC
Neolan Pink B	NC
Neolan Pink G	NC
Neolan Yellow G	NC
Neolan Yellow GR	NC
Patent Phosphine M	NC
Rhodamine B Extra	C
Romanowsky Stain	NC
Thio Indigo Red 3B Paste	NC
Trisulphon Bronze BG Conc	NC
Ultra Violet MO	NC
Xylene Blue VS Conc	NC
Xylene Fast Blue FF Conc	NC
Xylene Milling Blue AE Conc	NC
Xylene Milling Blue BL Conc	NC
Xylene Milling Orange R Conc	NC

JULY

Benzo Fast Scarlet 4BS	C
Indigosol O4B	NC
Methylene Blue Pure	NC
Neolan Blue B	NC
Romanowsky Stain	C

The Role of Chemistry in the Manufacture of Silk*

Raw Materials—Throwing—Degumming—Dyeing Procedure for Testing Dyes—Fastness Properties

By WALTER M. SCOTT

Cheney Brothers, South Manchester, Conn.

THE introduction of the technically trained chemist into the textile industry, and particularly into the silk branch of this industry, is a comparatively recent event. Fifty years ago no article could have been written on this subject—and, in fact, no one would have attempted to write such an article, because chemistry was not even thought of in connection with silk. Ten years ago the chemist had progressed far enough so that he was in a position at least to write an apology, defending his entrance into the silk industry chiefly from the standpoint of the number of problems waiting to be solved, and prophesying great things for the future. At the present time, although it cannot be truthfully said that we have arrived at a complete understanding of all the processes of silk manufacture, still we can, with a reasonable amount of pride in our profession, assert that the application of the principles of chemistry has pointed the way to the solution of a number of these problems.

At the very beginning the chemist had to possess more than the usual amount of temerity which is generally ascribed to him to expect to make any impression on an industry that had been in continuous operation since the dawn of history. We have authentic evidence that in the early ages the cultivation of the silk worm and the manufacture of silken fabrics were placed under the direct supervision of kings and emperors, and they were even dignified by occupying a space in the writings of the famous Chinese philosopher, Confucius, who lived about 500 B. C.

Ever since the beginning of time the processes involved in the manufacture of silk have been jealously guarded. In the early days in China the cultivation of silk was made part of a religious ceremonial and there was a penalty of death for anyone who divulged the secrets of the art to unauthorized persons. During the Middle Ages in Europe there were developed very powerful guilds of silk workers, to which a man was admitted only after many years of apprenticeship. Even fifty years ago the idea of handing down the secrets of the trade from father to son still persisted, particularly among silk dyers and finishers. These people were naturally opposed to having their formulas and processes analyzed and interpreted by an outsider, and equally so to making any radical changes in the methods that they had been using for many years.

Fortunately, an outside influence came to the aid of the

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chemist. The gradual development of synthetic dyestuffs during the past fifty years necessitated radical changes in dyeing procedure and paved the way for the scientifically trained man to work out new methods of application to fit the new types of coloring matters. Finally, the readjustments brought about by the World War, including the threatened famine of dyestuffs in the early years of the war and the gradual substitution of American types for the corresponding German ones, left the chemist more firmly entrenched than ever.

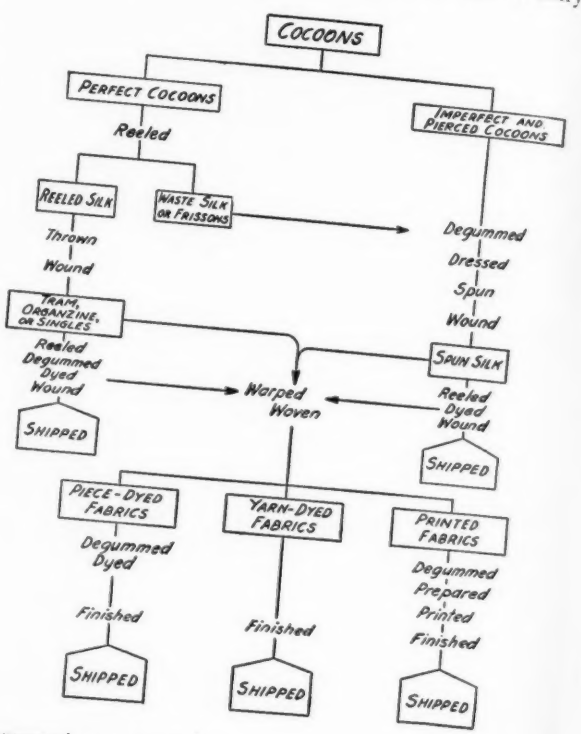
Naturally, the persons most interested in the advent of the chemist in the silk industry were the silk manufacturers themselves. They felt, and rightly so, that it was up to the chemist to show that his knowledge could be applied to their problems so as either to improve the quality of their goods or to decrease the cost of their production. The fact that more and more chemists are finding a place in this industry is a good indication of the value placed upon them at the present time by all progressive manufacturers. However, in order to give an intelligent idea of the contacts that have been established between chemistry and silk, we will now take up in detail the various processes that are involved in the transformation from fiber to fabric.

Raw Materials

Before starting upon what might be termed the career of the silk, let us pause for a moment to consider the constitution of the raw material. The pure silk fiber, which is called fibroin, is entirely covered with a protective coating of silk gum or sericin. It has been shown that these two compounds are very similar in their chemical nature, and that they belong to the protein group. The structure of the fibroin molecule has not yet been completely established, but all the evidence obtained so far indicates that it is a polypeptide—i. e., a complex combination of amino acids. The German chemist Abderhalden has succeeded in obtaining and identifying 86.4 parts of various amino acids, such as alanine, tyrosine, glycine, etc., from the hydrolysis of 100 parts of ash-free fibroin. If we consider the simplest polypeptide as an illustration—namely, glycyl-glycine, whose formula is $NH_2—CH_2—CO—NH—CH_2—COOH$—, we find that there is a free amino group, a free carboxyl group, and a —CO—NH— group. The higher polypeptides, such as fibroin and sericin, will naturally contain a large number of these groups.

A theory has been advanced by Speakman that the —CO—NH— groups are capable of existing in two forms: the keto form, —CO—NH—, and the enol form, —C(OH)=N—. The conversion from keto to enol form is reversible and is dependent on the hydrogen-ion concentration of the solution in which the protein is immersed. In acid solutions the keto form predominates and will combine with the acids present, while in alkaline solutions combination occurs with the enol form. The combined reactivity of the —CO—NH— groups and the free amino and carboxyl groups led Speakman to designate fibroin as doubly amphoteric. This theory will account for the behavior of the silk in a number of the processes to be discussed later.

A general idea of the various steps in the conversion of raw silk into silk yarns or fabrics may be obtained from the accompanying chart. Here is shown in graphic form the connection between the various processes which will be emphasized as being of particular interest to the chemist. Inasmuch as silk is not grown in this country, our connection with the fiber starts either with reeled silk, frissons, or imperfect cocoons.



Throwing

This is the first step in the transformation of the reeled silk which has been imported from the filatures of Japan, China or Italy. The operations of winding, reeling, twisting, etc., which come under this heading, are largely mechanical, but it has been found that their success depends in a large measure upon the effectiveness of the preliminary soaking bath. The skeins of raw silk are immersed in this bath, which consists of some form of oil emulsion, either cold or lukewarm, and then extracted and dried. The problem of the chemist is to provide an emulsion which will be stable and from which the silk will absorb an amount of oil to give it maximum pliability in the subsequent operations.

The standard formula which has been in use for a good many years consists of a combination of a good neutral soap with a saponifiable oil, such as neat's-foot or olive oil. More recently emulsions have been made with sul-

phonated oils of various sorts, and with specially prepared mineral oils. The latter will produce very fine emulsions, but they are not in very general use because of the difficulties encountered in later processes due to presence of the mineral oil. One firm has quite recently recommended producing an emulsion by the addition of an oil containing a certain amount of free fatty acid to a dilute solution of a mild alkali, such as potassium carbonate.

Degumming

The complete removal of the protective coating of sericin without injury to the fibroin or silk fiber is a problem of prime interest to the chemist. Sericin is soluble to a large extent in pure water, but cannot be completely removed by this agent unless treated under pressure at temperatures higher than 100 deg. Cent. It is entirely dissolved by mild alkaline solutions and, although somewhat less sensitive to acid, it is readily attacked in a moderately strong acid solution.

Some of the more common solutions which have been used in actual practice for the purpose of degumming silk are:

1. A solution of a neutral soap, usually made from olive oil or red oil.

2. Mixtures of soaps or soluble oils with some form of alkali, such as sodium carbonate, sodium perborate, trisodium phosphate, etc.

3. A solution of a strong alkali, such as caustic soda, which has been buffered by some agency, such as glucose or sulphite pulp liquor.

4. The addition of some organic solvent, such as carbon tetrachloride, to the degumming solution has been recommended.

The silk may be immersed in these solutions in an open vat or, less commonly, in an autoclave under pressure. In the former case the temperature is usually kept around 100 deg. Cent., but in the latter much higher temperatures may prevail. Where some type of soap solution is used, the silk is often not immersed but suspended above the boiling solution and is completely degummed by the action of the foam.

An entirely distinct method of removing the sericin is by the use of various types of enzymes. It has long been known that silk can be completely degummed by enzymes generated within itself, if left for a sufficient length of time in a lukewarm solution. This process was formerly employed by Cheney Brothers and produced a very fine quality of silk. It was finally discontinued owing to the strong objection of the workmen and the near-by residents to the very obnoxious odors which were liberated. Some of the common enzymes which have a satisfactory action on sericin are trypsin and pancreatin in a weak alkaline solution and pepsin in a weak acid solution. In all cases, however, it has been found advisable to complete the process with a short immersion in a dilute soap solution.

Dyeing

The function of the chemist in connection with the various processes included under this heading is pretty well defined. He must be familiar with all the types of dyestuff which might possibly be of interest to the plant where he is employed. In his study of each individual dye a large number of factors should be taken into consideration. To illustrate this, a typical procedure for the routine testing of dyestuffs in the laboratory of a silk mill is outlined below:

Standard Dyeing—The dyestuff is applied to the fiber or fabric in a definite proportion under standard conditions of solution, temperature and time, so as to produce maximum exhaustion of the bath.

Wash Test—A portion of the standard dyeing is immersed for ten minutes in a 0.5 per cent soap solution at 120 deg. Fahr.

Acid Test—Immersion for five minutes in a cold 1 per cent solution of sulphuric acid.

Alkali Test—Five minutes' immersion in a cold 1 per cent solution of sodium carbonate.

Water Test—Sixteen hours' immersion in cold water.

Light Test—Exposure on the roof under glass for a period equivalent to about fifty hours of June sunlight. A dyeing of a standard is always put out with each series of samples and the exposure is continued until this standard fades to a definite end point.

Standard Print Test—The dyestuff solution of standard strength is mixed with a definite amount of printing gum and then struck off on a small patch. In order to make the results of the various tests comparative, it is necessary to maintain uniform conditions in the drying, steaming and washing of these patches.

Wash Tests for Prints—A portion of the standard print is tested in a similar manner as the standard dyeing.

Discharge Test—The standard print is also tested for its fastness to a definite strength of sodium sulphoxylate formaldehyde. Again care must be exercised to apply the reducing agent in the same manner each time, and to maintain uniform conditions of temperature and moisture in the steam box.

As a result of these general tests, it is possible to separate the dyestuffs into a number of groups depending upon their dyeing characteristics and their fastness properties. If it is desired to produce a line of shades that are specially resistant to washing or to light, it is possible to pick out a limited number of dyestuffs which show no change in the general tests for fastness to these agencies. Then, by increasing the severity of the tests, further elimination can be made until there is left a much smaller number, which represents the best selection for the purpose.

In connection with this subject of fastness it is evident that the chemist has a very definite mission. He is the person who is best qualified to establish standard tests which will clearly define the various classes of fastness, so that everybody may arrive at a mutual understanding of the limitations of this much abused term. The American Association of Textile Chemists and Colorists, a comparatively new organization in this field, has realized its obligation in this matter and has already made excellent progress toward the standardization of tests for fastness to washing and to light. It is at present co-operating with the Bureau of Standards in exposing about one thousand different dyeings on cotton, wool and silk to varying amounts and qualities of light. As a result of these experiments they hope to be able to make some definite recommendations on this subject.

Turning from the question of fastness properties, it might be well to deal briefly with the classification of dyestuffs from the standpoint of application. The following summary of the more important classes will serve to point out the opportunities for a chemist in this field:

Acid Colors—The members of this group will dye silk in a strongly acid bath. In a paper presented before the last annual meeting of the Textile Chemists' Association* the author was able to show that the amount of acid dyestuff absorbed by silk from a solution of given initial concentration increases with the hydrogen-ion concentration of this solution; also that in dye baths acidified with acetic, sulphuric or hydrochloric acid, the amount of acid dyestuff absorbed by the silk at a given initial hydrogen-ion concentration of the solution is constant and is not dependent on the absolute amount of acid used to obtain this hydrogen-ion concentration.

The silk industry consumes a larger amount of acid colors than of any other type, because of the ease of application and the possibility of matching accurately a large number of shades particularly noticeable for their delicacy or brilliancy. In this group will be found certain dyestuffs which are distinguished by their fastness toward light and others which possess considerable fastness toward washing, but very few acid colors combine both of these fastness properties.

Basic Colors—The members of this group will dye silk either in a weakly acid, neutral or slightly alkaline solution. They are especially distinguished by their exceptional brilliancy of shade and usually possess good fastness toward washing, but are quite fugitive to light.

Direct Colors—The members of this group will also dye silk in a weak acid solution, but preferably in a neutral or slightly alkaline bath. With regard to fastness toward washing, there is some variation among the individual dyestuffs, but all possess a higher degree of fastness than the majority of acid colors. Certain of the direct colors are capable of being diazotized and developed on the fiber, whereby their fastness to washing is greatly improved.

The direct colors vary considerably in their fastness toward light, some of them being very good in this respect, so that it is possible by a careful selection to produce shades which will be satisfactory for many purposes. It is interesting to note that many of them are faster to light when dyed on silk than when dyed on cotton.

Vat Colors—The members of this group can only be dissolved in a fairly strong alkaline solution containing a reducing agent, such as sodium-sulphite ($Na_2S_2O_4$). If the alkalinity of the solution is too great, there will be very little affinity for the silk fiber. With this class of dyestuffs the problem is to reduce the alkalinity to the lowest point consistent with complete solubility of the dyestuff. In a number of instances the addition of sodium bicarbonate or some other buffer to the dyestuff solution is effective in increasing its affinity for the silk.

The popular conception of vat colors is that they are absolutely fast to every conceivable destructive agency. Unfortunately, this is not so, although it is true that as a group they are the fastest types of color known. However, it is just as necessary in this group to make a careful selection of individual types if it is proposed to guarantee the fastness of the dyed shades toward washing or toward light.

Conclusion

Considerably more space might be devoted to pointing out in detail some of the numerous other problems which engage the chemist in a silk mill, such as a study of the various gums used in printing, development of special preparations for finishing the goods, finding the best method of disposal for the trade wastes, etc. However, there has already been given sufficient evidence to prove that the chemist is a very important factor at the present time in the manufacture of silk. It is, without doubt, safe to predict that in the next fifty years there will be just as many revolutionary changes in the silk industry as in the fifty years that have just passed. It is also a foregone conclusion that the chemist will be even more intimately connected with these future changes than he has been with those in the past.

*American Dyestuff Reporter, 14, 862 (1926).

MOIRE EFFECTS ON CELLULOSE ACETATE

In British Patent No. 250,658, the British Celanese, Ltd., describe a process for producing moire effects on materials having cellulose acetate bases. Close line grid patterns are impressed on each side of the material to create opposite optical interference by the effect of the lines on opposite sides.

AMERICAN
DYESTUFF REPORTER

Devoted to the use and application of dyestuffs and the mechanical equipment incidental thereto.

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FORERUNNER OF WHAT?

THE address delivered by Irenee du Pont at the anniversary meeting of the American Chemical Society was entitled "The Dyestuffs Industry—Forerunner of What?" but Mr. Du Pont did not dwell very long on the subject of dyes. A brief quotation will serve to summarize the variety of apparently unrelated topics to which he alluded during the course of his speech:

> We all know that insignificant amounts of certain organic chemicals properly applied have wonderfully decreased the ravages of diseases and increased correspondingly the length of effective life.
>
> Attention has been called to the fact that small quantities of compounds of the accelerator class enormously increase the mileage of automobile tires at a comparatively trifling cost; that the use of tetraethyl lead will cause an enormous increase in the mileage per gallon of gasoline used in automobiles. . . . That new finishes have been obtained resulting in very large savings; that flotation agents have been obtained by which ores can be separated from their gangues; that the dyestuffs industry enables man to color his every product according to his desire. . . .
>
> We know that theoretically many millions of organic compounds may be prepared, each with different properties. Is it not likely then that there remain undiscovered compounds of even more surprising potentiality for the welfare of mankind?

From this point the speaker proceeded into a realm which has been described by some commentators as fantastic. He discussed the possibilities of future chemical marvels, such as synthetic starches and sugars, anti-corrosion chemicals and, most striking of all, certain stimulating drugs which will do away with the necessity of sleep, create genius and change character.

To the lay mind he may seem to have digressed often and deviated quite aimlessly from his original subject. As a matter of fact, Mr. Du Pont's breadth of mind led him to see far beneath the dye industry to its deeper significance and to its foundation, the science of organic chemistry. Dye manufacture is but a branch of that science, but it claims some distinction because it was the first important branch to appear in this country. He tried to show us that if we had not established a dyestuff industry ten years ago we should not have one of organic chemistry to-day, and that we should not thus be able to look so far into the future and contemplate some of the things which he believes lie within the pale of possibility. He tried to show us that a limitless field was opened when our pioneer dye manufacturers first set up their plants to meet the needs of the hour, never dreaming, perhaps, that they were laying the groundwork for numberless scientific discoveries far more important than dyes to the welfare of mankind.

If his remarks are considered in this light—that the dye industry is acting only as the forerunner of many incredible discoveries—his address is seen to be a convincing argument for the maintenance and support of coal tar chemical research. His panegyric on organic chemistry comes at a time when our dyestuff industry is celebrating the completion of its first decade and he was therefore able to give specific instances of what has been achieved in the past ten years and from those draw a conception of what is to come.

The lesson is plain: heretofore we have been too much absorbed in the commercial aspects of dyestuff production. We have not always brought to our enterprise that spark of imagination which is slowly turning our organic chemical industry into an infinite source of synthetic products even more wonderful than some of those suggested by Mr. Du Pont. As Dr. Armstrong of the British Dyestuffs Corporation declared, "A new Aladdin's lamp is in the hands of the chemist!" But if it is used only to light the way to material fortune its latent powers will never be realized. Because Irenee du Pont considers the sociological rather than the commercial phase, he is able to see more in organic chemistry than most of us.

COLLECTING THE LITERATURE OF DYEING

IN the chemical industries, and in technical libraries where compiling is done, there is always a place for men with a thorough knowledge of the technical literature covering various branches of chemistry. Some of the principal qualifications of a "literature

technologist" were recently outlined by a German chemist, Dr. Bugge, who suggested that more chemists might find it profitable to turn their attention to the possibilities of such a vocation. A literature technologist must have, first of all, a fundamental theoretical training, several years of practical experience and a reliable memory, if he would be a fully capable authority on the technical literature of his special calling. He must also possess, according to Dr. Bugge, versatility and mental mobility; these to give him a thorough acquaintance with the most varied problems and a wide perspective of the whole field of technology. But on second thought it would seem to us that in this type of work the specialist ought to be more successful than the voracious scholar who spreads his interests over an extensive field of scientific knowledge. There is in this thought something for the mill chemist or dyer who has a penchant for collecting technical articles.

Although the wet processing of textiles may be considered as a comparatively narrow field, the published literature on the subject would undoubtedly fill a small library. Statisticians may be able to tell us the precise height of the pile this printed literature would make in comparison to the Woolworth Building or some similar lofty structure. And it is continually increasing, since a number of independent studies and investigations are always being carried on in each division of the science. Current periodicals, both American and foreign, publish countless volumes of reports of dyeing tests on all classes of textiles, studies of every existing class of dyestuffs and detailed descriptions of all types of processing machinery. We have scholarly researches into the chemistry of fibers, exhaustive explanations of bleaching and finishing methods, of water softening systems, of calico printing, and warp sizing and singeing; whole reams of reading, in short, for beginner and experienced worker alike. Much of it may be put aside merely as so much printed matter; but a certain proportion, each year, forms a valuable contribution to our technical knowledge.

The mill chemist or dyer cannot hope to know more than a small fraction of this literature. His time for reading is limited and no matter how studious he may be he cannot devote all of that time to technical reading. But would it not be worth his while to make a systematic collection of the technical literature in which he is particularly interested, for the purpose of future reading or for reference?

Suppose, for example, that one were to start a file on some specific subject, not too broad—such as cotton piece goods bleaching—and slowly to branch out into related studies, adding to the file all new material sufficiently valuable to save for reference. Would not that be a simple way to acquire a reputation in the mill as a literature technologist on the subject of dyeing? A dyer or chemist who kept such a file of information would soon have a home-made ready reference encyclopedia on subjects directly related to his daily work. He would unquestionably be more valuable to his employer, and would very often have the great personal satisfaction of being able to solve his dyeing problems more quickly than the man who relied entirely on his own experience.

GERMAN DYE HEADS COMING HERE

Representatives of the German dye cartel, comprising a group of leading executives of the various German dye companies, will arrive in the United States during the next two weeks, according to a recent cable from Berlin. The group will include Dr. Bosch, president of the Badische Company, who will sail from Hamburg on the Columbus; Dr. Walter Duisberg and Fritz Termeer, who will sail on the Reliance on Sept. 21, and Councillor Schmitz and others on the Majestic on Sept. 28.

NEW SULFOGENE COLOR

The Dyestuffs Department of E. I. du Pont de Nemours & Co. announces a new sulphur dye, Sulfogene Olive G, which is offered as a particularly valuable color in combinations for producing sulphur khakies of exceptional fastness. When extreme fastness is to be obtained by aftertreatment with chrome, copper and acetic acid, Sulfogene Olive G is especially good because there is said to be practically no change in the shade of dyeings of this color when thus aftertreated.

IMPORTS OF ANILINE OIL AND SALT INTO CANADA

Although Canada's imports of aniline oil declined in 1925, the United States continued to be the chief source of the supply, shipping 151,600 pounds of the Dominion's total importation of 163,000.

Imports of aniline salt were 70 per cent greater in 1925 than in 1924. Of a total of 12,000 pounds received, 7,000 came from the United States.

UNITED STATES EXPORTS NAPHTHALENE TO NEW ZEALAND

The United States became a source of New Zealand's imports of naphthalene in 1925, when it exported to that country a quantity valued at £117. New Zealand's total importation of the product amounted to £1,206 in the past year, nearly double the 1924 receipts. The United Kingdom enjoys the bulk of this trade.

The Dyestuffs Industry, Forerunner of What?*

Measuring Dyestuff Progress—Volume of Manufacture—Variety of Products—Dye Selling Prices—Rubber Accelerators—Anti-knock for Gasoline—Contribution to Metallurgy—Prevention of Rust—Effects on Humans—The Reward of Research—Government and Chemistry

By IRENEE DU PONT

Vice-Chairman of Board, E. I. du Pont de Nemours & Co.

SOME seven years ago the American Chemical Society, at its meeting in Philadelphia, passed the following resolution:

Whereas the establishment of a complete self-contained coal-tar chemical and dye industry is a national necessity because of its well-defined character as a key industry in our economic life; and

Whereas this industry has a much deeper significance in that it constitutes a vital reserve both as to personnel and supplies for our Army and Navy in modern warfare; and

Whereas this industry is also essential for supplies of synthetic drugs for the health of the Army, Navy and general public in peace and in war; and

Whereas this country possesses an abundance of raw material for such an industry, ample capital and chemists capable of solving the many scientific and technical questions involved, as evidenced by the splendid progress of the past three years; and

Whereas this initial period, with all of its attendant difficulties, has not yet been adequate to admit of the efficient production in domestic plants of all colors needed by American consumers; and

Whereas the greatly depreciated rate of exchange in that country which in the past has manufactured the bulk of the world's supply of dyes presents a new and threatening factor in all transactions of an international character: Therefore be it

RESOLVED, first, That we urge all Americans to stand loyally by the young industry which embodies such far-reaching potentialities of service and protection for our country;

Second, That every needful safeguard be thrown around this industry by the Congress of the United States, especially through the imposition of effective import duties and the provision of a temporary licensing system along the general lines embodied in H. R. 8078, known as the Longworth bill.

Correct.

CHARLES L. PARSONS, *Secretary.*

It seems, therefore, appropriate to review, in the light of the years which have elapsed, the progress made in the dye industry, and also the progress made in analogous chemical industries, which progress is dependent on the same character of reactions, apparatus and personnel as the dye industry.

Progress in the dye industry can be broadly measured by a comparison of—

1. The volume of manufacture measured in pounds.
2. The variety of products made.
3. The selling prices of the dominating items.

For this purpose it seems proper to choose for the comparison the years—

1914, largely before the World War, when the United States was dependent on Germany for its supplies of dyestuffs.

1919, immediately after the World War, which had caused a period of five years of substantially complete embargo of the importation of dyes.

1925, the most recent year available after a period of tariff protection.

VOLUME OF MANUFACTURE

The following table is from data of the United States Department of Commerce; the figures are in units of 1,000 pounds and take no cognizance of the improvement in tinctorial power in the products in the later periods:

(In units of 1,000 pounds.)

	1914	——1919——		——1925——	
	Imports	Production	Imports	Production	Imports
Acid	9,286	12,196	....	10,214	590
Basic	3,002	4,036	....	4,122	608
Direct	10,264	14,445	....	14,788	759
Lake and spirit soluble	1,512	1,813	....	1,606	58
Mordant and chrome	4,450	3,985	24	2,543	642
Sulphur	7,054	17,624	....	20,760	122
Indigo	8,407	8,864	1,051	29,122	2
Other vats	1,945	389	2,215	2,608	2,417
Unclassified	27	49		581	12
	45,947	63,401	3,290	86,344	5,210

*An address before the American Chemical Society's Golden Jubilee Meeting, Philadelphia, September 6, 1926.

It takes but a cursory examination of these figures to show that the complete embargo for the years 1914 to 1919 resulted in the establishment of a real dyestuffs industry in the United States, and that so far as tonnage is concerned the dyestuffs industry has not made commensurate progress during the period when tariff protection was relied on for its stimulation. It is quite striking to point out, however, that in the case of Indigo and sulphur colors, which have a low selling price and are protected by a prohibitive tariff, satisfactory growth has continued.

In the case of vat colors the tariff protection has not been sufficient to enable American manufacturers to produce the country's requirements; and, in fact, 1925 importations were 75 per cent greater than those for 1924 as a result of the reduction in tariff from 60 per cent to 45 per cent ad valorem in September, 1924.

Variety of Products

From the best data obtainable the Du Pont company believes that there were made in the year 1914 about 104 different dyes, and these largely from imported intermediates; in 1919, it is estimated, there were 250 types of dyes manufactured; in 1925 the estimate is at least 350 different dyes. This, too, indicates that the embargo due to the World War fostered progress in developing the art in this country. The apparent lessening progress since is partly due to the approach of the "saturation point" with respect to the number of dyes actually required in industry and partly to an effort to eliminate inefficient and needless dyes.

From both these comparisons it appears that the resolution of the American Chemical Society, above referred to, was well warranted from the point of view of the dyestuffs manufacturing industry. Now let us consider whether it has been a burden on the users of dyes and, therefore, on the ultimate consumer of goods requiring dyestuffs. It would require too much space to enumerate the corresponding prices on every dye that is sold. To group them by classes would be misleading, because of the interchangeability of many dyestuffs with different values. However, there are dominant dyes comprising a large proportion of the total tonnage which are comparable for the different periods.

Dye Selling Prices

The table below gives the current selling prices for the period 1913-1914, the year 1919 and the year 1925. The prices given in columns 2, 3 and 5 are for an amount of the dye which would give tinctorial power equal to a pound of the dye as sold in the earlier year. Columns 4 and 6 have been added, being respectively 58 and 59 per cent of the corresponding figures in columns 3 and 5 to allow for the shrinkage in purchasing power of the dollar in the latter periods. The purchasing power of the dollar, 58 cents for 1919 and 59 cents for 1925, represents its average purchasing power as measured by the cost of living in average American communities as published by the National Industrial Conference Board.

These data clearly disprove the claim made by certain importers that embargo or high tariff would put an undue financial burden on the user or consumer of dyes.

	1913–1914 Price	1919 Price		1925 Price	
——(1)——	(2)	(3)	(4)	(5)	(6)
Indigo 20 Per Cent Paste	$0.15½	$0.75	$0.43½	$0.14	$0.08¼
Sulphur Black, pre-war type, single strength	.17	.20	.11½	.11–.12	.07
Direct Deep Black E Extra	.20	1.00	.58	.33	.19½
Agalma Black 10BX	.27	1.45	.84	.54	.32
Orange II Conc	.16	.63	.36½	.29	.17

Supplementary Materials

Closely related to dyestuffs are certain other organic materials which are of great importance in that they supplement the dyestuffs industry, broadening its scope and giving a greater horizon for future discovery. Without boring you with comparative tabulations showing the growth of these, let it be said that the total amount made in the United States in 1914 was negligible, whereas for the year 1925 we have the following imposing business:

Product	Sales—Pounds	Sales—Value	Production, Pounds
Photographic chemicals	349,000	$475,000	327,000
Medicinals	3,295,000	6,332,000	3,238,000
Flavors	2,149,000	1,409,000	2,207,000
Perfumes	2,371,000	884,000	2,335,000
Synthetic tanning materials	13,897,000	8,699,000	14,687,000
Synthetic phenolic resins			

After this general view of the situation, let us take up some specific accomplishments which are outstanding from a commercial point of view.

Rubber Accelerators

One of the most notable is that class of compounds known as rubber accelerators. In 1906 Oneslager discovered that aniline had an accelerating action in the curing of rubber, but for a decade little attention was paid

to its possibilities. Then came discoveries of less poisonous materials of greater power, until in 1925 we find that there were produced in the United States for this purpose:

Diphenylguanidine	1,204,700	pounds
Thiocarbanilide	2,352,000	"
Triphenylguanidine	494,100	"
Hexamethylenetetramine	1,658,000	"

These compounds not only have the property of hastening the curing process in the manufacture of rubber goods, but to a considerable extent improve the quality of the rubber into which they have been incorporated. Dr. W. C. Geer, in his paper read before the American Chemical Society a little over a year ago, states that these chemicals were saving the American public at the rate of $50,000,000 per annum and by their speeding up manufacturing processes have saved the rubber manufacturers $80,000,000 additional capital investment which would otherwise have been required.

One of the large rubber companies has made an estimate that the increased mileage of tires made with accelerators over the mileage which would have been obtained without such ingredients has in the last ten years aggregated 240,000,000,000 tire miles, or equivalent to sending 2,500,000 automobiles around the world at its equator. The total cost of these accelerators has been but a small fraction of the value of the results obtained.

Anti-Knock for Gasoline

Another outstanding accomplishment is the invention of the so-called anti-knock for gasoline used in internal combustion engines. It is well known that the thermal efficiency of an internal combustion engine increases quite rapidly with the degree of initial compression put upon the mixture of fuel and air before its ignition, and that, unfortunately, when a pressure is reached which is quite definite for any particular fuel, the nature of the explosion in the engine suddenly changes, producing what is known as a "knock"; that this knock is occasioned by a nearly instantaneous and very high-pressure explosion in which a large proportion of the energy is given out as radiant energy to be absorbed by the walls of the cylinder and, therefore, not available for mechanical work on the crankshaft. The critical pressure which induces a knock is far below that which could be easily obtainable mechanically.

Thomas Midgley, of the Dayton Engineering Laboratories, in his investigation of the cause of "knocking," discovered that adding small amounts of certain compounds to the fuel materially changed the pressure at which knocking was produced. He finally found tetraethyl lead, whose properties in this regard are quite astonishing. Amounts as small as one-twentieth of 1 per cent of the fuel are ordinarily sufficient to permit an increase of 50 per cent in the initial compression, with a corresponding increase in the efficiency of the motor using it. It is now certain that the mileage of automobiles per gallon of gas can be increased 50 per cent by its use. Consequently, one-third of all gasoline used can be saved by the use of this compound. If it had been universally applied in the year 1925 this would have resulted in a saving of some three billions gallons of gasoline. One may reasonably expect that this saving actually will be obtained within a very few years. It will, of course, require changes in automobile design.

New Variety of Lacquer

Another extraordinary use of organic compounds is the combination of certain organic solvents with nitrocellulose to form a new variety of lacquer. In the last two years finishes of this kind have largely supplanted coach paints and varnishes for finishing automobiles, and are making rapid inroads in many other industries. I am advised by one automobile body manufacturing company that if such lacquers had not been available they would have had to spend $10,000,000 for additional paint shops and drying equipment to take care of the increase of their business in the last two years. For commercial reasons, presumably, they have not divulged the economy in operation, though it is known to be very large. The great value of the invention has been to the ultimate consumer (the automobile owner), because this class of finish will outlast two or three applications of the old-fashioned type. This not only reduces the average per annum cost of repainting but the car is in the paint shop less often and, because of the rapid drying of the new finish, is out of use for a much shorter time.

Contribution to Metallurgy

Possibly many of you do not appreciate the extent that organic chemistry has contributed to metallurgy. The process known as "Flotation" started with the use of coal-tar oils, which could be had at a very low cost. It has been more recently discovered that mixtures of certain purified organic reagents, such as alphanaphthylamine and xylidine and, later, thiocarbanilide and orthotoluidine, secured more accurate selection of the desired ores from the pulverized run of mine. Still more recently potassium xanthate has taken the lead for this purpose. The dyestuffs industry was peculiarly able to supply these reagents in large quantities at reasonable costs. Data from twenty-five leading mining companies producing copper in the year 1925 indicate that 63 per cent of their output, or 1,481,000,000 pounds, was produced by the aid of flotation.

We all know that insignificant amounts of certain organic chemicals properly applied have wonderfully decreased the ravages of disease and increased correspondingly the length of effective life. Attention has been called above to the fact that small quantities of compounds of the accelerator class enormously increase the mileage of automobile tires at a comparatively trifling cost; that the

use of tetraethyl lead will cause an enormous increase in the mileage per gallon of gasoline used in automobiles, and this, too, at an insignificant cost; that new finishes have been obtained resulting in very large savings; that flotation agents have been obtained by which ores can be separated from their gangues; that the dyestuffs industry enables man to color his every product according to his desire—surely as great a diversity of benefits as could well be imagined.

We know that, theoretically, many millions of organic compounds may be prepared, each, with different properties. Is it not then likely that there remain undiscovered compounds of even more surprising potentiality for the welfare of mankind? Without wishing to appear visionary, let us consider a few possibilities:

Effect on Fuel Supply

Experimental research has already developed a possibility of making liquid fuels for internal combustion engines which will take the place of gasoline should the supply of this fuel become exhausted; this through the route of high-pressure synthesis of carbon monoxide and hydrogen to form methanol; and, in fact, this synthesis of methanol is being successfully accomplished on a commercial scale in Germany. The same new tool, high-pressure synthesis, has in the laboratory made hydrocarbons. It is therefore hardly a prophecy to say that this will be commercialized for the benefit of the human race. The synthesis of starches and sugars may be reasonably expected to follow at a more distant date.

Using Energy of Sun

The use of the radiant energy of the sun as a source of power has long been a problem substantially unsolved. A few experimental sun-heated boilers have been operated, but no real commercial success has been attained. Nature's laboratory in the leaves of plants proves that radiant energy can be stored through the use of organic reactions. Is it not reasonable, then, to suppose that this problem particularly fits solution by the organic chemical route, and would it not seem equally reasonable to suppose that reactions will be found far more efficient than those provided by nature in growing vegetation? Bear in mind, the solution may be one with a deferred yield of either light or electricity.

Prevention of Rust

It is estimated that corrosion of iron is proceeding the world over at a rate about equivalent to the rate that iron is manufactured in Great Britain. Alloys, known as rustless steel, have already been made, but they are too expensive for use where cost per unit is important. Is it out of the question to find an organic material which can be absorbed into the pores of the iron itself, or possibly forced into them, which will then have the property of preventing the formation of the oxide?

Antidote for Sleep

We know that some adults sleep more hours per night than others. It seems likely that this is due to some slight differences either of the nature of more quickly accumulated poisons which necessitate sleep for their removal or a less rapid elimination of these poisons by those who sleep less efficiently. Would it not seem also likely that the reactions may be hastened by some catalytic agent or even that the antidote itself may be prepared and administered, thereby either decreasing the amount of sleep required or even doing away with the necessity of sleep entirely? It is interesting to note here that I asked Professor Steiglitz his view on such an apparently absurd question. His reply was that it would be like having a fire without a chimney—perhaps a cryptic answer, especially as we have seen in recent years the introduction of the electrical resistance furnace and more lately the induction furnace, both of which do operate without a chimney. Such a discovery could add some 50 per cent to both our hours of production and our hours of leisure and by its complete accomplishment would greatly decrease the cost of housing and the capital cost per unit of production of all those factories which to-day do not operate on a twenty-four-hour schedule.

Effect on Humans

Certain drugs tend to stupefy and prevent humans from thinking clearly; other drugs, such as caffein, as usually taken in tea and coffee, surely to some extent stimulate the mind, with apparently no corresponding later depression. Is it not reasonable to suppose that there exist other compounds which might stimulate the mind to greater extent so that mentally all the users would become supermen or geniuses? Would not research with this end in view be worth while, in view of the advantage to humanity were it successful and thereby all men became intelligent and alert?

You must have experienced in your lifetime cases where most lovable characters as they grew older became crabbed, intolerant, melancholy or in some other way deteriorated. It is proverbial that if one's liver is out of order it definitely does affect one's outlook on life for the worse, and there can be no question that the liver's function is essentially a chemical one. You probably have observed cases where children after an operation for adenoids or defective tonsils have become much less bashful, have improved in their studies, have become more cheerful—in short, have become brighter. It seems reasonable to suppose that they had been troubled by some secretion affecting their mental processes. Other organs and glands presumably have analogous effects, so much so that it does not seem to be unreasonable to suppose that one's character itself is the result of the sum total of certain chemical reactions taking place in the body. When the nature of these is understood, may we expect that by injecting proper compounds into an individual we can make

his character to order? If study and experiment can reach this result, it would seem to be a short cut to the millennium.

Why has not greater progress been made in devising new uses for organic compounds? It would seem to me clear that the main cause is the time required for making experiments; especially where effect on human beings is concerned, experimentation apparently becomes extremely slow. We can speed up a given experiment a little, but not much. Improvement in this regard must lie in carrying on multiple experiments by an army of trained observers. Trained observers are surely learning to reduce their observations to writing so that others may compile the results with the work of their fellows. To my mind this is the portal to the rapid progress which will be made in the future.

Insufficiency of Reward

It will astonish some of you if I say that insufficiency of reward is delaying progress. Our patent system is designed to reward progress and doubtless has been of great aid, but does the inventor and pioneer really get a reward adequate to stimulate research and the application of research to a degree commensurate with the enormous benefits to humanity?

In a case, the details of which are known to me personally, a company employed men for several years and finally brought out a new product which saved the public many millions of dollars. Out of each $100 saved by the invention $97 was passed to the public, $2.70 was passed to the pioneer company and only 30 cents to the men doing the work in recognition of their success. The particular case is probably fairly representative, though the public believes that both the company and the men have been most generously rewarded.

Why didn't the company charge a greater profit on the novelty? Purely because imitations immediately appeared and consumers would give no material preference to the original article. If the public would willingly pay a reasonable price for an article that saves it money, we would doubtless find a more rapid increase in the development of inventions.

Progress is dependent on painstaking experiments and observations which require time and money. We are living in a period when wealth has enormously increased, and which is, therefore, well adapted for the making of progress. Indications are that the application of the scientific practices already known will materially increase this surplus wealth which is available for research, and that this in turn can furnish the means to make faster progress in the future. However, prosperity can be easily upset. If those opposed to the capitalistic system were to come into power in our government, the creation of wealth would decrease so rapidly that research progress would be throttled.

It may not seem germane to the subject to point out to you that notwithstanding the phenomenal gain in knowledge in chemistry and other natural sciences, there has been no corresponding gain in the science of government. In fact, an unprejudiced spectator might say that even here in the United States we are retrograding. We have given up our republic and taken on a democracy. We determine by popular vote how ends should be accomplished rather than what ends should be accomplished. Our Representatives and Senators in Congress are instructed by their constituents how to vote on questions. What hope would there be of advancement in chemical research or the applications of research to production if the method of application was voted on by the populace? Is lawmaking, then, so simple that the average mind is more expert than specialists? This question is propounded here because, to my mind, the greater danger to further and phenomenal progress in chemistry is degeneracy in government.

Let the public, then, do their part by selecting the best men available to represent them in our government; let those engaged in chemical industry invest more freely in research, and especially reward more liberally the successful scientist. Let the chemists themselves be even more frank in disclosing the results of their work to their fellows, thereby obtaining the good results of teamwork. You may rest assured that the dyestuffs industry will then prove to be the forerunner of the chemistry of human well-being.

TEXTILE DYEING

(*Continued from page* 606)

dye and how to produce various shades. This innovation was not received kindly by the old dyer, who felt that his secret was a stock in trade as to his methods. Therefore, many of the published processes were hidden away and the names of the dyes were scratched from the labels on the packages in the dispensing room. To prevent the spread of knowledge as to what was transpiring, fictitious names were frequently substituted on these packages. Indeed, a great deal of this old attitude still remains among dyers of the old school, but modern dyers realize that no one can know too much and that real danger lies in knowing something that is not so. The modern dyer seeks to promote accuracy and avoid mistakes, so that he not only leaves the proper names on the packages but prepares a full list of the dyes in use in his dyehouse, printing these on slips of paper so that the weights of dyestuffs required for starting or maintaining a dye bath can be written opposite the colors to be used.

With a long list of dyes made available by chemistry came the realization that with the proper adjustment of proportions any shade between white and black may be produced and most of them with the three primary colors, red, blue and yellow. Now, when a new shade is to be dyed, the colors having the required fastness are selected and the laboratory boy

is assigned the task of working out the correct proportions for the dyer. He often prepares more formulas in a week than the old-fashioned dyer ever knew.

One might conclude that the influence of chemistry has robbed the dyer of some of his prerogatives, but this is not the case, for he has become more of an artist and less of an artisan. His function is to produce as nearly as possible a perfect match for the shade specified. The minute differences between shades cannot be weighed, so that now, as always, the exact final adjustments must depend upon the judgment and skill of the dyer.

Equipment

These epoch-making contributions of chemistry led to the invention of machines in which cotton fiber could be handled and the centrifugal extractors for removing excess water or dye solution, replacing the laborious winch. Then came the continuous running machines for drying the dyed fiber, and after this instead of the revolving carrier which alternately immersed the cotton and drained it, there came the static machine. In this machine the fiber lies quiet while the water or dye liquor is circulated, thus avoiding matting and leaving the fibers in good condition for subsequent processes of manufacture. A natural result has been a change in the dyehouse from hand workers to machine tenders, with a reduction in labor cost and an improvement in uniformity and quality.

To-day in addition to the circulating machines, wherein the fiber is quiet and the solutions move, we have the dyeing of wool in the fiber in similar machines, and the dyeing of yarn in packages, as beams and spools. Even cloth is wound on perforated drums and dyed in continuous dyeing machines. To-day one may see a continuous stream of cotton pass from picker to cards to dye machine to drier and to the final carding machines. A set of warps wound on perforated beams may enter the dyehouse in the morning, be dyed a red, for example, fully equal to the old Turkey red, go through the dress room, and be on the looms the same day. Contrast this with the half-hundred handlings and the weeks of time required fifty years ago. The changes are due to chemistry.

Changes in the dyeing of wool and woolen fabrics, silk and silk fabrics, and the printing of textiles correspond with those in cotton dyeing, though in some cases the fundamental differences in the fibers have meant less radical changes in apparatus, modes of application, and labor involved.

Dyeing of Artificial Silk and Wool

By the introduction, on a commercial scale, of artificial silk, acetate silk and artificial wool, the chemist has for the first time given the dyer fresh materials to dye. The older types (all are very recent) of artificial silk presented no grave difficulties, except that they called for special handling by the dyer. Viscose and all products of this type dye very readily, and they are dyed by the same colors which are suitable for cotton. On the other hand, the fiber is tender when wet and it must be handled so as to retain the beautiful gloss which is its most striking characteristic. It is different with acetate silk. In this the fiber refuses to take any of the ordinary dyestuffs except the basic colors, and the basic colors, though very beautiful, are extremely fugitive. Therefore, the chemist has been called upon to produce a totally new type of dyestuff for the specific purpose of dyeing this new fiber. In this he has succeeded and we have an excellent range of colors for acetate silk which are all new and allow of producing very interesting and beautiful effects.

In an up-to-date dyehouse nothing is done just as it was fifty years ago; the improvement is almost entirely to the credit of the chemist.—Industrial and Engineering Chemistry.

The rate for "Position Wanted" advertisements in this column is 2 cents a word—with a minimum of 50 cents per insertion. For all other types of advertisements—i. e., help wanted, machinery or supplies for sale—the rate is $5.00 per column inch or less per insertion.

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Textile chemist and colorist, 33 years of age, desires responsible position in laboratory, dyehouse or printshop. Twelve years' thorough experience on wide variety of fibers, fabrics and dyes, particularly fast colors. Excellent references. Reply Box 352, American Dyestuff Reporter.

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Hotels

Rates are from $1.50 to $5.00 for one person and from $5.00 to $8.00 for two persons depending upon the hotel. There are four to choose from, Hotel Charlotte being the headquarters for the meeting.

Railroad Fares

We will get special rates from the railroad company. The larger the party going the better will be the rate, therefore, we can only give you definite advice as to amount after we know how many will go.

Official Meetings of the Association

These will consist of an open forum on Friday evening and all-day sessions on Saturday.

Side Trips

The committee of arrangements in the South has tentative plans for a number of plant visits or other interesting occupations for one or two days prior to the meeting. These plans are dependent entirely upon what **you** want so that any who would like to make some of these side trips should indicate it at the earliest moment.

Returning

The railroad company will have the same sleepers available for our return.

Please do not postpone your decisions but indicate to the committee now your intention of being one of the party.

———COMMITTEE———

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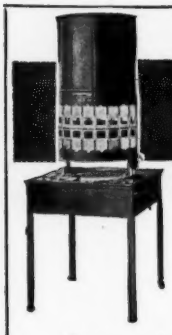

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